Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): Hydrazine EC Number(s): 206-114-9 CAS Number(s): 302-01-2

Submitted by:European Chemical Agency on request of the European CommissionVersion:February 2011

PUBLIC VERSION: This report does not include the Confidential Annexes referred to in Part II.

CONTENTS

PI SU	ROPO JBST	SAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, VPVB C ANCE OF AN EQUIVALENT LEVEL OF CONCERN)R A 7
P	ART I		8
Л	JSTIF	ICATION	8
1	IDE	NTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES	8
	1.1	Name and other identifiers of the substance	8
	1.2	Composition of the substance	9
	1.3	Physico-chemical properties	9
2	HAI	RMONISED CLASSIFICATION AND LABELLING	11
3	ENV	/IRONMENTAL FATE PROPERTIES	12
4	HUN	MAN HEALTH HAZARD ASSESSMENT	13
5	ENV	/IRONMENTAL HAZARD ASSESSMENT	14
6	CON	NCLUSIONS ON THE SVHC PROPERTIES	15
	6.1	PBT, vPvB assessment	15
	6.2	CMR assessment	15
	6.3	Substances of equivalent level of concern assessment.	15
P	ART I	I	16
IN	FOR	MATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS	16
1	EXE	ECUTIVE SUMMARY	16
	1.1	Manufacture, Imports and Exports	16
	1.2	Uses	16
	1.3	Releases from Manufacture and Use	17
	1.4	Current Knowledge of Alternatives	19
2	PUF	RITY AND DIFFERENT FORMS OF HYDRAZINE	21
	2.1	Purity of Anhydrous Hydrazine	21
	2.2	Solutions of Hydrated Hydrazine	22
3	INF	ORMATION ON MANUFACTURE, IMPORT, EXPORT AND RELEASES FROM MANUFACTURE.	22

ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

	3.1	Production Process	22
		3.1.1 The Olin Raschig Process	22
		3.1.2 The Atofina-PCUK (Peroxide) Process	23
		3.1.3 The Bayer (Ketazine) Process	23
		3.1.4 The Hoffmann (Urea) Process	24
	3.2	Production Sites	
		5.2.1 EU Flouderion Sites	
		3.2.2 Non-EU Production Sites	
	3.3	Production Volumes	25
		3.3.1 Historical Information – Global Production	25
		3.3.2 Current EU Production	25
	3.4	Imports into the EU	25
	3.5	Future Trends	25
	2.6		24
	3.6	Information on Releases from Manufacture	
		3.6.1 Releases to the Environment from Manufacture	
		3.6.1.1 Information from Literature	
		3.6.1.2 Consultation Findings	
		3.6.2 Releases to the Working Environment and Occupation Exposure during Manufacture	
		3.6.2.1 Information from Literature	
		3.6.2.2 Consultation Findings	27
4	INF	ORMATION ON USES OF HYDRAZINE	
			• •
	4.1	Overview of Hydrazine Uses	
		4.1.1 Possible Uses referred to in Literature	
		4.1.2 Hydrazine Hydrate vs. Hydrazine Derivatives	
		4.1.3 Information on Overall Use Patterns (Tonnage)	
		4.1.3.1 Information from Literature – Historical Information on Global Consumption	
		4.1.3.2 Consultation Findings – Current Information on EU Consumption	
	4.2	Use in Syntheses	
		4.2.1 Introduction	
		4.2.2 Pharmaceuticals and Agrochemicals	33
		4.2.3 Chemical Blowing Agents	33
		4.2.4 Polymerisation Initiators and Catalysts	34
		42.5 Crosslinking in Urethanes and Acrylics	34
		4.2.6 Lubricants	
		4.2.7 Nuclear Reactor Waste Treatment	
	4.3	Use in Water Treatment	
		4.3.1 Description of Use	
		4.3.1.1 Background (including Information from Literature)	
		4.3.1.2 Consultation Findings	37
		4.3.2 Locations and Quantities Used	41
		4.3.2.1 Industry Sectors Potentially using Hydrazine Hydrate	41
		4.3.2.2 Locations of Power Generation Plants	41
		4.3.2.3 Locations of Other Potential Users	41
		4.3.2.4 Quantities Used	42
		4.3.3 Recent and Future Trends	43
		4.3.4 Structure of Supply Chain	
	44	Use as Reducing Agent for Metals	44
		441 Description of Use	
		4.4.1.1 Information from Literature	-11 41
		4.4.1.2 Consultation Findings	
		1.1.1.2 Constitution 1 mangs	

	4.4.2	Locations and Quantities Used	48
	4.4.3	Structure of Supply Chain	49
4.5	Use ir	n Effluent Treatment	49
	451	Description of Use	49
		4.5.1.1 Information from Literature	49
		4512 Consultation Findings	49
	152	Locations and Quantities Used	/0
	4.5.2	Decarbon and Quantities Osci	40
	4.5.5	Structure of Supply Chain	49
	4.3.4		49
16	Use ir	Daint Ink and Dya Manufactura	50
4.0		Use in Daint and Ink Manufacture	50
	4.0.1	Use of Hydrogrino (Dhanyilhydrogrino og a Dyilding Dlagk of Organia Dyag	50
	4.0.2	Use of Hydrazine/Filenyinydrazine as a Bunding block of Organic Dyes	50
17	Use ir	Durification Applications	50
4./	Use II	r furnication Applications	50
19	Use ir	A grospage Applications	51
4.0	101	Description of Use	51
	4.0.1	4.8.1.1 Information from Literature	51
		4.8.1.1 Information from Literature	51
	400	4.8.1.2 Consultation Findings	52
	4.8.2	Locations and Quantities Used	52
	4.8.3	Recent and Future Trends	53
	4.8.4	Structure of Supply Chain	53
4.9	Use in	Defence Applications	53
	4.9.1	Description of Use	53
		4.9.1.1 Information from Literature	53
		4.9.1.2 Consultation Findings	54
	4.9.2	Locations and Quantities Used	55
		4.9.2.1 Fighter Jet Emergency Power Units	55
		4.9.2.2 Submarine Rescue System Gas Generators	56
	4.9.3	Structure of Supply Chain	56
4.10	Other	Uses	57
	4.10.1	Use in Syntheses of Unclear Relevance to the EU	57
		4.10.1.1 Photography Chemicals	57
		4.10.1.2 Anti-oxidants	58
		4.10.1.3 Flame Retardants	58
		4.10.1.4 Oil Stimulation Agents	58
	4.10.2	Use in Shipping	58
	4.10.3	B Use in the Recovery of Gold from Ores	58
		4.10.3.1 Information from Literature	58
		4.10.3.2 Consultation Findings	59
	4.10.4	Use in the Semiconductor Industry	59
		4.10.4.1 Information from Literature	59
		4.10.4.2 Consultation Findings	60
	4 10 5	5 Use in Vehicle Fuel Cells	60
		4 10 5 1 Information from Literature	60
		4 10 5 2 Consultation Findings	60
	A 10 6	Vise in Soldering Fluxes	61
	- .10.0	4 10 6 1 Information from Literature	61
		4.10.6.2 Consultation Findings	61
	4 10 7	4.10.0.2 Consumation Finances and Ampunition Propallants	61
	4.10./	4 10 7 1 Information from Literature	61
		4.10.7.2 Consultation Fordings	01
	4 1 0 0	4.10.7.2 Consultation Findings	02
	4.10.8	Use in Automotive Air Bag Gas-forming Agents	62
		4.10.8.1 Information from Literature	62
		4.10.8.2 Consultation Findings	63

ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

	4.11 Other Information – Member State Authorities		63	
	4.12	Sumn	nary of Use	63
5	REI	LEASE	S FROM USES OF HYDRAZINE	74
	5.1	Relea	ses to the Environment	74
		5.1.1	Use in Water Treatment	74
			5.1.1.1 Information from Literature	74
			5.1.1.2 Consultation Findings	75
			5.1.1.3 Conclusion	76
		5.1.2	Use as a Reducing Agent for Metals	76
			5.1.2.1 Production of Precious Metals	76
			5.1.2.2 Production of Basic Metals	76
		5.1.3	Use in Aerospace Applications	
		5.1.4	Use in Defence Applications	
			5.1.4.1 Fighter Jet Emergency Power Units	
		515	5.1.4.2 Submarine Rescue System Gas Generators	
		5.1.5	Releases from Other Applications	
	5.2	Relea	ses to the Working Environment	78
		5.2.1	Dilution and Distribution of Hydrazine Hydrate	78
			5.2.1.1 Information from Synthesis	
			5.2.1.2 Modelled Exposure	
		5.2.2	Use in Water Treatment	80
			5.2.2.1 Information from Literature	
			5.2.2.2 Consultation Findings	
		523	Use as a Reducing A gent for Metals	
		5.2.5	5 2 3 1 Information from Literature	82
			5.2.3.2 Consultation Findings	
			5.2.3.3 Modelled Exposure	
		5.2.4	Use in Aerospace Applications	
			5.2.4.1 Information from Literature	
			5.2.4.2 Consultation Findings	85
			5.2.4.3 Modelled Exposure	
		5.2.5	Use in Defence Applications	
			5.2.5.1 Information from Literature	86
			5.2.5.2 Consultation Findings	
			5.2.5.3 Modelled Exposure	
6	CUI	RRENT	۲ KNOWLEDGE ON ALTERNATIVES	
	6.1	Alteri	natives for Water Treatment	
	0.1	6.1.1	Availability and Identities/Description of Alternatives	
			6.1.1.1 Alternative Substances	
			6.1.1.2 Comparison of Alternative Substances	
			6.1.1.3 Alternative Techniques	95
		6.1.2	Practical Experience of EU Stakeholders with Alternatives	96
		6.1.3	Limiting Factors for the Uptake of Alternatives	
		6.1.4	Requirements for Future Work on Alternatives	
	6.2	Alteri	native Reducing Agents for Metals	
		6.2.1	Alternatives for Metal Deposition	
			6.2.1.1 Availability and Identities/Description of Alternatives	100
			6.2.1.2 Practical Experience of EU Stakeholders with Alternatives	
		6.2.2	Alternatives for the Production of Precious Metals	
			6.2.2.1 Availability and Identities/Description of Alternatives	
			6.2.2.2 Practical Experience of EU Stakeholders with Alternatives	
		6.2.3	Alternatives for the Production of Basic Metals	

6.3	Alternatives for	r Effluent Treatment	
	6.3.1.1	Alternative Substances	
	6.3.1.2	Consultation Findings	
6.4	Alternative Ae	prospace Propellants	
	6.4.1 Availab	bility and Identities/Description of Alternatives	
	6.4.1.1	Recent EU Research on 'Green' Propellants	
	6.4.1.2	Recent Research outside the EU	
	6.4.1.3	Availability and Identities/Description of Alternative Monopropellants	
	6.4.2 Practica	al Experience of EU Stakeholders with Alternatives	
	6.4.2.1	Alternatives based on Ammonium Dinitramide	
	6.4.2.2	Alternatives based on HAN, Hydrogen and HNF	
	6.4.3 Limitin	g Factors for the Uptake of Alternatives	
6.5	Alternatives for	or Submarine Rescue Systems	116
	6.5.1 Availab	vility and Identities/Description of Alternatives	116
	6.5.2 Practica	al Experience of EU Stakeholders with Alternatives	117
	6.5.3 Limitin	g Factors for the Uptake of Alternatives	117
6.6	Information or	1 Similar Substances that may act as Substitutes	
	6.6.1 Substitu	ution Scenarios	117
	6.6.1.1	Replacement by Salts	117
	6.6.1.2	Interchangeability of Anhydrous and Hydrate Forms	118
	6.6.1.3	Replacement by Derivatives	118
	6.6.2 Compa	rison on Hazard Characteristics and Toxicity of Hydrazine and Selected Substitutes	
7 REI	FERENCES		
ANNE	X 1. OCCUPA	FIONAL EXPOSURE ESTIMATION ASSUMPTIONS	
ANNE	X 2. CONFIDE	NTIAL INFORMATION ON MARKETS AND USES	
ANNE	X 3. CONFIDE	NTIAL INFORMATION ON RELEASES	149
ANNE	X 4. CONFIDE	NTIAL INFORMATION ON ALTERNATIVES	150

TABLES

Table 1.1: Substance identity	
Table 1.2: Constituents	
Table 1.3: Impurities	
Table 1.4: Additives	
Table 1.5: Overview of physicochemical properties	
Table 2.1:Classification according to part 3 of Annex VI, Table 3.1 ((list of harmonised classification and labelling of	
hazardous substances) of Regulation (EC) No 1272/2008	
Table 2.2: Classification according to part 3 of Annex VI, Table 3.2 (list of harmonized classification and labelling of	
hazardous substances from Annex I of Council Directive 67/548/EEC)11	
Table 2.1: Specifications of Commercial Anhydrous Hydrazine 21	
Table 3.1: Occupational Exposure to Hydrazine in the USA - Production and Derivative Manufacture (historical data	
reported in 1986)	
Table 4.1: Examples of Possible Applications for Hydrazine and its Derivatives - Results of Literature Search28	
Table 4.2: Range of Hydrazine Hydrate and Derivatives and Relevant Applications 30	
Table 4.3: Hydrazine Global Usage Patterns - 1960s to 2000s	
Table 4.4: Description of Hydrazine Hydrate Use as a Corrosion Inhibitor in Power Plants - Company 26	
Table 4.5: Past and Future Trends in Consumption of Hydrazine Hydrate for Water Treatment (Corrosion Protection)	_
Selected Companies	
Table 4.6: Potential Uses of Hydrazine (and its Salts) in Electroless Metal Plating	

ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

Table 4.7: Composition of Hydrazine Gas Generator Propellants for the Submarine RESUS System	54
Table 4.8: Number of Active F-16 Fighter Jets in EU/EEA Countries	
Table 4.9: Classes of Submarines that may contain Hydrazine Gas Generators (RESUS)	
Table 4.10: Data on the Swedish Market for Hydrazine and its Mixtures – 2009	03
Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU	64
Table 5.1: Hydrazine Concentration in Effluent from Nuclear Power Plants of Ontario, Canada	74
Table 5.2: Releases and Transfer of Hydrazine to Japanese Environmental Media $(t/y) = 2001$	77
Table 5.3: Patterns of Occupational Exposure to Hydrazine during Supply and Distribution of Hydrazine Hydra	ite –
	/8
Table 5.4: Occupational Exposure Levels for Workers of UK Plants Processing and Distributing Hydrazine Hydr	drate
Solutions	79
Table 5.5: Modelled Estimates for Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous Hydrazine)	lrazine)
– Use in Closed Systems (100% solutions)	80
Table 5.6: Patterns of Occupational Exposure to Hydrazine during the Use of Hydrazine Hydrate in Power Stati	ions
(estimated 90 sites) – UK, 2006.	81
Table 5.7: Consultation Results on Worker Exposure from Use of Hydrazine Hydrate in Water Treatment	81
Table 5.8: Modelled Estimates for Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous Hyd	razine)
– Use in Closed Systems (55% and 5% solutions)	82
Table 5.9: Estimated Occupational Exposure to Hydrazine during its Use in the Production of Basic Metals (Se	lenium
Process, Finland, Company 27)	83
Table 5.10: Estimated Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous Hydrazine) –	
Preparation and Use of Electroless Plating Baths (open systems)	83
Table 5.11: Occupational Exposure to Hydrazine in the USA – Aerospace Applications (1986)	85
Table 5.12: Measured Occupational Exposure during the Use of Anhydrous Hydrazine in the Manufacture of T	hrusters
(Company 25)	85
Table 5.13: Modelled Estimates for Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous	
Hydrazine) – Use of Anhydrous Hydrazine (>99%) in Aerospace Applications	86
Table 5.14: Occupational Exposure to Hydrazine in the USA – Fighter Jet Applications (1986)	87
Table 5.15: Modelled Estimates for Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous	
Hydrazine) – Use of Anhydrous Hydrazine (70%) in Defence Applications	89
Table 6.1: Overview of Alternative Corrosion Inhibitors (Substances)	89
Table 6.2: Reaction and Breakdown Products of Selected Alternative Oxygen Scavengers	93
Table 6.3: Comparison of Key Properties of the Main Oxygen Scavenger Substances	93
Table 6.4: Alternative Reducing Agents for Electroless Deposition of Nickel	100
Table 6.5: Alternative Reducing Agents for Gold Refining in the Aqua Regia Process	102
Table 6.6: Alternative Reducing Agents for Effluent Treatment	104
Table 6.7: Expertise and Research on 'Green' Propellants for Spacecraft within Europe (2008)	105
Table 6.8: Comparison of Toxicities of Hydrazine, ADN and HAN (rat, oral)	107
Table 6.9: Properties of ADN-based Monopropellants	108
Table 6.10: Comparison of Toxicity Data of HNF Blends to Hydrazine and Hydrogen Peroxide Propellants	111
Table 6.11: Composition of Gas Generator Propellants for the Submarine RESUS System	116
Table 6.12: Comparison of Hazard Classification of Hydrazine and Selected Hydrazine Derivatives	118
Table 6.13: Lethality (LC ₅₀) of Hydrazine and Methylated Hydrazines in Rodents	
Table 6.14: Comparison of Past Test Results on the Toxicity of Hydrazine. MMH and UDMH	122
Table A1.1: Modelling Assumptions and Estimates of Inhalation Exposure during the Use of Anhydrous Hydra	zine 138
Table A1.2: Modelling Assumptions and Estimates of Dermal Exposure during the Use of Anhydrous Hydrazir	12.139
Table A1.3: Modelling Assumptions and Estimates of Inhalation Exposure during the Use of Hydrazine Hydrat	e in
Closed Systems	142
Table A1.4: Modelling Assumptions and Estimates of Dermal Exposure during the Use of Hydrazine Hydrate i	n
Closed Systems	
Table A1.5: Modelling Assumptions and Estimates of Inhalation Exposure during the Preparation and Use of	
Electroless Plating Raths containing Hydrazine Hydrate	145
Table A1.6. Modelling Assumptions and Estimates of Dermal Exposure during the Preparation and Use of Flee	troless
Plating Baths containing Hydrazine Hydrate	147

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, VPVB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): Hydrazine

EC Number(s): 206-114-9

CAS number(s): 302-01-2

This dossier covers the anhydrous hydrazine, EC number 206-114-9 and CAS number 302-01-2, and all its possible hydrates.

• The substance is proposed to be identified as a substance meeting the criteria of Article 57 (a) of Regulation (EC) 1907/2006 (REACH) owing to its classification as carcinogen category 1B⁻¹ which corresponds to classifications as carcinogen category 2²

Summary of how the substance meets the CMR (1A or 1B) criteria

Hydrazine is covered by index number 007-008-00-3 of Regulation (EC) No 1272/2008 in Annex VI, part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) as carcinogen, Carc. 1B (H350: "May cause cancer"). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised and classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen, Carc. Cat. 2, R45 ("May cause cancer").

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as carcinogen in accordance with Article 57 (a) of REACH.

Registration dossiers submitted for the substance? Yes

¹ Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances.

² Classification in accordance with Regulation (EC) No 1272/2008, Annex VI, part 3, Table 3.2 List of harmonised classification and labelling of hazardous substances (from Annex I to Council Directive 67/548/EEC).

PART I

JUSTIFICATION

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1.1:Substance identity

EC number:	206-114-9
EC name:	Hydrazine
CAS number (in the EC inventory):	302-01-2
1. CAS number: hydrate(s)	7803-57-8
2. CAS number (alternate):	10217-52-4
3. CAS number: deleted	119775-10-9; 75013-58-0; 78206-91-4; 31886-26-7
CAS name:	Hydrazine
IUPAC name:	Hydrazine
Index number in Annex VI of the CLP Regulation	007-008-00-3
Molecular formula:	H_4N_2
Molecular weight:	32 g/mol
Synonyms:	H70; H70 (fuel); Levoxine; Nitrogen hydride(N2H4); Oxytreat 35

Structural formula:



1.2 Composition of the substance

Name: Hydrazine

Degree of purity: 93 - 100 %

Table 1.2:Constituents

Constituents	Typical concentration	Concentration range	Remarks
Hydrazine 206-114-9		93 – 100 %	Based on the information received in the registration dossiers

Table 1.3:Impurities

Impurities	Typical concentration	Concentration range	Remarks

Table 1.4:Additives

Additives	Typical concentration	Concentration range	Remarks

1.3 Physico-chemical properties

Property	Value	Remarks
Physical state at 20°C and 101.3 kPa	Colorless liquid with an ammoniacal odor	Ullmanns Encyclopedia of Industrial Chemistry, Hydrazine, Jean-Pierre Schirmann, Paul Pourdauducq, Wiley-VCH Verlag GmbH & Co. KHaA, Weinheim, 2005
Melting/freezing point	2.0 °C	Lide, David, R., Handbook of Chemistry and Physics, 75 th Edition, CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1994- 1995
Boiling point	113.5 °C at 760 mmHg	The Merck Index, 14 th Edition, Merck & Co., Inc., Whiterhouse Station, NJ, USA, 2006
Vapour pressure	1.91 kPa at 25 °C	Lide, David, R., Handbook of Chemistry and Physics, 75 th Edition, CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1994- 1995
Water solubility	<i>Miscible with water in all proportions</i>	Ullmanns Encyclopedia of Industrial Chemistry, Hydrazine, Jean-Pierre Schirmann, Paul Pourdauducq, Wiley-VCH Verlag GmbH & Co. KHaA, Weinheim, 2005
Surface tension	66.7 mN/m at 25 °C (c = pure substance)	Ullmanns Encyclopedia of Industrial Chemistry, Hydrazine, Jean-Pierre Schirmann, Paul Pourdauducq, Wiley-VCH Verlag GmbH & Co. KHaA, Weinheim, 2005
Partition coefficient n- octanol/water (log value)	<i>logPow</i> = -2.07 <i>at</i> 25 ° <i>C</i>	ECHA, calculation according to EPISUITE performed with the module WSKOWWIN, 2011
PK _a value	8.1 at 25 °C	Lide, David, R., Handbook of Chemistry and Physics, 75 th Edition, CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1994- 1995
Viscosity	$0.974 \ \mu Pa.s \ at 20 \ ^{\circ}C$ ($c = pure \ substance$)	Ullmanns Encyclopedia of Industrial Chemistry, Hydrazine, Jean-Pierre Schirmann, Paul Pourdauducq, Wiley-VCH Verlag GmbH & Co. KHaA, Weinheim, 2005
Flash point	52 °C	Lide, David, R., Handbook of Chemistry and Physics, 75 th Edition, CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1994- 1995

 Table 1.5:
 Overview of physicochemical properties

2 HARMONISED CLASSIFICATION AND LABELLING

Hydrazine is covered by Index number 007-008-00-3 in Annex VI, part 3 of Regulation (EC) No 1272/2008 as follows:

Table 2.1:	Classification according to part 3 of Annex VI, Table 3.1 ((list of harmonised
classification	and labelling of hazardous substances) of Regulation (EC) No 1272/2008

Index No	Internatio	EC No	CAS No	Classificat	tion		Labelling		Spec.	Notes
	nal Chemical Identificat ion			Hazard Class and Category Code(s)	Hazard state- ment code(s)	Pictogr am, Signal Word Code(s)	Hazard state- ment code(s)	Suppl. Hazard stateme nt code(s)	Conc. Limits, M- factors	
007-008-00-3	HYDRAZI	206-114-9	302-01-2	Flam. Liq3	H226	GHS02	H226		Skin	
	NE			Carc. 1B	H350	GHS06	H350		Corr. 1B;	
				Acute Tox. 3*	H331	GHS08	H331		H314: C≥ 10%	
				Acute Tox. 3*	H311	GHS05	H311		Skin Irrit.	
				Acute Tox. 3*	H301	GHS09	H301		2;	
				Skin Corr. 1B	H314	Dgr	H314		H315: 3% ≤ C< 10%	
				Skin Sens. 1	H317		H317		Eve Irrit	
				Aquatic Acute 1	H400		H410		2; H319:	
				Aquatic Chronic 1	H410				3% ≤ C < 10%	

Table 2.2:	Classification according to part 3 of Annex VI, Table 3.2 (list of harmonized
classification	and labelling of hazardous substances from Annex I of Council Directive
67/548/EEC)	

INDEX NO	INTERNATI ONAL CHEMICAL IDENTIFICA TION	EC NO	CAS NO	CLASSIFICAT ION	LABELLING	CONCENTRATION LIMITS	NOTES
007-008-00-3	HYDRAZINE	206-114-9	302-01-2	R10 CARC. CAT.2; R45 T; R23/24/25 C; R34 R43 N; R50-53	T; N R: 45-10- 23/24/25-34- 43-50/53 S: 53-45-60-61	C; R34: C ≥ 10% XI; R36/38: 3% ≤ C < 10%	Е

3 ENVIRONMENTAL FATE PROPERTIES

4 HUMAN HEALTH HAZARD ASSESSMENT

5 ENVIRONMENTAL HAZARD ASSESSMENT

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 **PBT**, vPvB assessment

6.2 CMR assessment

Hydrazine is covered by index number 007-008-00-3 of Regulation (EC) No 1272/2008 in Annex VI, part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) as carcinogen, Carc. 1B (H350: "May cause cancer"). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised and classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen, Carc. Cat. 2, R45 ("May cause cancer").

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as carcinogen in accordance with Article 57 (a) of REACH.

6.3 Substances of equivalent level of concern assessment.

PART II

The underlying work for development of Part II of this Annex XV report was carried out under contract ECHA/2010/174 SR27 by DHI³ in collaboration with Risk & Policy Analysts Limited⁴ and TNO⁵.

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

1 EXECUTIVE SUMMARY

1.1 Manufacture, Imports and Exports

Anhydrous hydrazine is not currently manufactured in the EU. Hydrazine hydrate is manufactured in two plants, located in France and Germany. The production method used differs between the two plants. The combined production tonnage is confidential and is in the 10,000-100,000 t/y range.

Non-EU manufacturing sites for hydrazine hydrate are located in Japan, China and Korea. Anhydrous hydrazine may be produced in the USA, Japan, China and potentially India and Russia. Open literature (from 2007) suggests a worldwide market demand for hydrazine hydrate of 80,000-90,000 t/y.

Hydrazine is imported into the EU in both its hydrated and anhydrous forms with the latter accounting for only a very small fraction of overall imports, estimated to be below 10 t/y. Imports of hydrazine hydrate are suggested to be much more significant than this, but such imports still account for a relatively small fraction of the overall EU market for the hydrated form.

1.2 Uses

Hydrazine, especially in its hydrated form, finds a wide range of applications in the EU, most of which fall under the "synthesis" heading; the key implication of this is that the substance (in its hydrated form) finds wide use as an intermediate, as defined under the REACH Regulation.

The applications that have been identified as currently relevant to the EU include:

- in its hydrated form (in solution concentrations ready for end-use between 3% and 100%):
 - synthesis of hydrazine derivatives these may act as or find uses in products such as pharmaceuticals, agrochemicals, chemical blowing agents, paints, inks and organic dyes, reagents for the treatment of nuclear reactor waste, and others (literature provides details of a large range of different applications for derivatives, salts, etc. of hydrazine);

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- use as a monomer in polymerisations (mostly for polyurethane coatings and adhesives);
- use as a corrosion inhibitor in water treatment, mainly for the removal of dissolved oxygen and the adjustment of pH in the feedwater of boilers as well as for the removal of solids from steam generators. The critical area of application are nuclear and thermal power generation plants (including water steam circulation for district heating and cooling). However, oxygen scavenging based on hydrazine is relevant for other industry sectors that utilise steam such as paper mills, steel manufacture, production of chemicals but not food generation;
- use as a reducing agent in the deposition of metals (nickel, chromium, tin and precious metals) on plastics and glass;
- use as a reducing agent in precious metal and basic metal recovery from metallic salt solutions and effluents;
- use as a reducing agent in purification of chemical reagents;
- use as a stabilising agent in aromatic amines (for subsequent paint/ink manufacture);
- use as a laboratory chemical reagent;
- in its anhydrous form (at high purity levels, >90%):
 - use as a propellant for aerospace vehicles (satellite propulsion and upper stages of satellite launchers);
 - use as a fuel in military (emergency) power units (for the F-16 fighter jets); and
 - use in gas generators for submarine rescue systems.

Aggregated (and largely confidential) data would suggest the following rough breakdown of current uses in the EU:

- use in synthesis and as a monomer in polymerisations reactions: ca. 80%;
- corrosion inhibitors, metal reduction, refining of chemicals: ca. 20%; and
- others (including anhydrous hydrazine and laboratory uses): <1%.

1.3 Releases from Manufacture and Use

Manufacture: confidential information has been provided by the two key EU manufacturers of hydrazine hydrate. It appears that some release to the atmosphere and the aquatic environment is possible but the companies' calculations indicate no risk for the environment in light of existing Risk Management Measures. In relation to occupational exposure, hydrazine is claimed to be highly contained and, as such inhalation exposure is limited to the $\mu g/m^3$ level.

Uses: information is not available for all identified uses of hydrazine and a significant proportion of information provided by industry stakeholders has been suggested to be commercially sensitive and is only available in Confidential Annex 3 of the report). Processes such as the dilution of hydrazine hydrate solutions, water treatment, metal reduction of precious metals, transfer and loading of anhydrous hydrazine in the aerospace sector may take place within closed systems. Such closed systems are evidently very important for installations such as the steam generators in nuclear and fossil-fired power plants, industrial plants reducing metallic salts to high purity precious metals intended for use in the electronics and catalysts industries and the fuelling of satellites ready for launching. Often the solutions used are very dilute too (for instance, this may be the case in oxygen scavenging and precious metal reduction).

On the other hand, for occupational exposure, modelling has been undertaken to estimate the potential for inhalation and dermal exposure under different scenarios. The results are shown in the following table.

 Table A: Overview of Modelled Inhalation and Dermal Exposure Estimates for Applications of Hydrazine (values as anhydrous hydrazine)

				Inhalatior	1 exposure	Dermal	exposure
Application	Typical fraction in product	Use of closed systems	Duration (mins)	Exposure parameter ¹	Estimated value (mg/m ³)	Exposure parameter	Estimated value (mg/kg bw/day)
Dilution	64%	Yes	15	RWC for task with RPE (90%)	0.058	Exposure with PPE	0.44
			180	RWC full shift with RPA (90%)	0.002-0.064	(90%)	
Water	5-55%	Yes	15	RWC for task with RPE (90%)	0.003-0.032	Exposure with PPE	0.021-0.24
treatment			180	RWC full shift with RPA (90%)	0.003-0.036	(90%)	
Electroless	0.01-3%	No	15	RWC for task with RPE (90%)	<0.001-0.14	Exposure with PPE	<0.001-0.45
plating			480	RWC full shift with RPA (90%)	<0.001-0.17	(90%)	
Precious metal	5-55%	Yes	15	RWC for task with RPE (90%)	0.003-0.032	Exposure with PPE	0.021-0.24
reduction			180	RWC full shift with RPA (90%)	0.003-0.036	(90%)	
Aerospace (filling of satellites)	100%	Yes	15	RWC for task with RPE $(90\%)^2$	0.09	Exposure with PPE $(90\%)^2$	0.69
Defence (filling of fighter jet EPU)	70%	Yes	15	RWC for task with RPE $(90\%)^2$	0.064	Exposure with PPE (90%) ²	0.48

Notes:

1 RWC: reasonable worst-case; RPE: respiratory protection equipment; PPE: personal protective equipment

2 For aerospace and defence applications, the types of RPE and PPE used is expected to be more sophisticated, for example, self-contained suits with independent air supply (Self-contained Atmospheric Protective Ensemble (SCAPE) suits) which may offer a removal rate of 97.5% leading to an exposure 4 times lower than the modelling estimates shown above

It should be noted that hydrazine is a very reactive reducing agent, and its wide use largely relies on this characteristic. Industry consultees have advised that hydrazine normally fully reacts or breaks down (typically to N_2 , H_2 , H_2O and NH_3 , depending on reaction conditions). However, the presence of a small residual concentration of hydrazine in the final product of polymerisation reactions (to give polyurethane resins) has also been brought to our attention.

1.4 Current Knowledge of Alternatives

The analysis of alternatives has largely focused on the three main applications areas outside the "REACH intermediates" field, i.e. corrosion inhibitors, metal deposition, reduction and recovery, and uses of anhydrous hydrazine in the aerospace and defence sectors.

Alternative corrosion inhibitors: literature and consultation has revealed a wide range of potential alternative substances, which could, theoretically, act as corrosion inhibitors for the treatment of boiler feedwater. Substances commonly referred to include diethyl hydroxylamine (DEHA), carbohydrazide, methyl ethyl ketone (MEKO), salts of isoascorbic acid, several filming amines, oxalates, formic acid, hydrogen and others. Of them, those that appear to be most promising (and are already used in certain situations) are DEHA and carbohydrazide. Some alternative techniques have also been suggested including (a) catalytic reduction in combination with the addition of alternative pH regulators and (b) the combination of improved water treatment with ammonia injection.

Alternative substances do not come without problems. Several of them contribute CO_2 and organic acids to the feedwater (the latter affecting the cation conductivity of steam and condensate) and their dosage is higher compared to hydrazine hydrate, on occasion by a large margin. Certain of the identified alternatives may offer no passivation of metallic surfaces (which hydrazine offers) while some may be accompanied by sluggish kinetics (and need to be supported by catalysts). It appears that many industry stakeholders have tested alternatives in the past. The results have not been satisfactory, especially in the power generation sector that has shown a particular interest in this study due to the key role of hydrazine hydrate solutions to ensuring the good and safe operation of power plants. Many consultees (including the relevant industry association, Eurelectric), have voiced strong support for the continued use of hydrazine hydrate solutions. Especially in relation to nuclear power plants, the use of hydrazine hydrate has been linked by consultees to the safeguarding of the integrity and safety of these facilities. Even where the onus of legislation (the Seveso II Directive) could instigate or promote the replacement of hydrazine hydrate by alternatives (such as carbohydrazide), power plants have apparently preferred to significantly reduce the concentration of solutions and the amount stored on-site rather than move to such alternatives, especially where large power plants are concerned.

Alternative reducing agents for metal deposition: for metallic (electroless) deposition, alternatives to hydrazine hydrate may include substances such as sodium hypophosphite, sodium borohydride, dimethylamine borane and N-diethylamine borane. For the plating of plastics, hydroxylammonium compounds and hydroxy acids may be used to replace hydrazine. Industry does have experience with these chemicals and it appears that hydrazine has largely been replaced but some 'pockets' of resistance to change may still exist across the EU.

For precious metal recovery from solutions and effluent streams, sodium borohydride and formic acid and its salts have been mentioned by consultees, while literature refers to products based on polypropylene or viscose backbones grafted with specific functional groups that can selectively remove precious metals from solution. However, hydrazine appears to be a better performing, well-controllable reducing agent with good selectivity and efficiency of the reaction. Formic acid and formiates in particular are very hard to control in comparison to hydrazine and have resulted in serious accidents in the past. Polypropylene/viscose-based systems may only be used effectively for metal removal from weak solutions.

Alternative aerospace propellants: literature sources and consultees suggest that the key alternative technologies are those based on ammonium dinitramide (ADN), hydroxylammonium nitrate (HAN) and hydrogen peroxide. The first two are reasonably recent developments; the first was developed in Sweden as part of a wider drive towards greener propellants in the EU aerospace industry – the second is currently being researched in the USA. Hydrogen peroxide is believed to be a somewhat 'older' technology.

ADN-based monopropellants (two different formulations developed in Sweden) have already found some practical experimental use. The PRISMA mission was recently launched on ADN-based fuel and results so far appear to be satisfactory. ADN-based formulations are less hazardous than anhydrous hydrazine, are claimed by their developers to have good compatibility with materials currently used in commercially available thrusters and can deliver a significant (up to 30%) increase in density-specific impulse over anhydrous hydrazine. However, they do require product re-design for thrusters with a thrust level above 1 N. In addition, ignition needs to be further explored; hydrazine propellants use catalytic ignition, which is simple and reliable. To replace hydrazine, an ADN-based monopropellant must be as easy to ignite. The high combustion chamber temperature is a matter of concern since it might deteriorate a catalyst bed.

The European Space Agency but also leading organisations and companies involved in Europe's space programme have voiced strong concerns on the readiness of ADN-based propellants to replace hydrazine even in the longer term, whilst the use of hydrazine is based on extensive research and experience over the last 50-60 years. The Agency in particular has expressed the opinion that no alternative to hydrazine in propulsion is available in the long-term and emphasised that the secured supply of hydrazine is vital for the current and future success of the European space programme. Experience with the performance of a propellant on a geostationary satellite is a prerequisite before it is considered a feasible alternative and such testing would require at least 15 years. Issues of the autonomy, strategic position and competitiveness of the European aerospace industry should also be taken into account. Additional comments on the potential shortcomings of ADN-based alternatives are provided in Confidential Annex 4.

Alternative gas generator fuels for submarine rescue systems: alternatives based on solid fuels such as a combination of glycidyl-acido-polymer and strontium nitrate are available on the market.

Structurally similar substances as potential alternatives: carbohydrazide has been identified as a potential alternative for corrosion inhibitor applications. The substance does not have a hazard profile as adverse as hydrazine (e.g. no cancer classification), although during use, it will partly break down to give hydrazine. Such breakdown takes place within closed systems where exposure of workers is not possible. On the other hand, some exposure might occur during solution preparation, as carbohydrazide may be available as a solid powder.

Monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) are methylated hydrazine derivatives that find wide use (especially MMH) in rocket propellants, however, typically as bipropellants (i.e. in the presence of an oxidiser). MMH appears to be more toxic than hydrazine while UDMH is somewhat less toxic but still carries a R45, Carc. Cat 2 classification. These substances have limited relevance as potential direct alternatives for hydrazine given that hydrazine is mostly used as a monopropellant.

Confidential Annex 4 contains information on certain alternatives already trialled by industry stakeholders.

2 PURITY AND DIFFERENT FORMS OF HYDRAZINE

2.1 Purity of Anhydrous Hydrazine

6

It is understood that anhydrous hydrazine that is used by the EU aerospace sector needs to comply with the US standard MIL-PRF-26536E⁶. This standard describes the purity grades of anhydrous hydrazine as shown in **Table 2.1**.

Table 2.1: Specifications of Commercial Anhydrous Hydrazine							
Component (% hy weight)	Grade						
	Standard	Monopropellant	High purity				
Hydrazine, min (%)	98.0	98.5	99.0				
Water, max (%)	1.5	1.0	1.0				
Particulate, max (mg/L)	10	1.0	1.0				
Ammonia (%)			0.3				
Aniline, max (%)		0.50	0.003				
Carbon dioxide, max (%)		0.003	0.003				
Chloride, max (%)		0.0005	0.0005				
Iron, max (%)		0.0004	0.0004				
Non-volatile residue, max (%)		0.005	0.001				
Other volatile carbonaceous material [*] , max (%)		0.02	0.005				
Source: US Air Force (1997) * total as unsymmetrical dimethyl h	nydrazine (UDMH),	monomethyl hydrazine (Ml	MH), and alcohol				

EU users of anhydrous hydrazine for aerospace applications require "high purity" grade which has a hydrazine content above 99%. We are advised that the "high purity" grade gives only a minimum specification, i.e. the factual purity of this grade is normally higher than 99.0%. Indeed, **Company 25** imports a small amount of anhydrous hydrazine from a Chinese manufacturer for own use in spacecraft propulsion and this has a reported purity of 99.9%.

The purity of anhydrous hydrazine used in marine rescue systems needs to be particularly high too. This is quantified and discussed in more detail in Confidential Annex 2 to this report. On the other hand, the hydrazine used in F-16 fighter jets (see discussion in Section 4.9.1) is a mixture of 70% hydrazine-30% water (also known as H-70).

The grades of hydrazine propellant described therein match those described in standard ISO 15859-7: 2004.

2.2 Solutions of Hydrated Hydrazine

Hydrazine has a molecular weight of 32 and the monohydrate has a molecular weight of 50. The ratio of their weight is 32/50 or 0.64. Therefore, a 100% monohydrate solution would contain 32/50 or 64% hydrazine. This is the reason for which 100% hydrazine hydrate can be used interchangeably with 64% contained hydrazine by weight (Arch, 2010f).

Hydrazine hydrate can be used in solutions of a very variable concentration. It is understood that a (relatively small) number of chemical distributors are involved in the dilution of high-concentration hydrazine hydrate solutions (with deionised water) into a range of different concentrations which are then supplied to downstream users across the EU. The Internet site of a UK company provides details on this: it appears that the company starts from a 100% hydrazine hydrate solution (equivalent to 64% anhydrous hydrazine) and then it prepares the following 'off the shelf' grades: 5%, 7.5%, 24%, 35%, 55%, 64% and 80% (with an equivalent anhydrous hydrazine concentration of 3%, 5%, 15%, 22%, 26%, 35%, 38% and 51%) (Lansdowne Chemicals, 2010).

The concentration of the final solution used by an end-user may vary depending on the nature of the application involved. Whilst some detailed information is given in Confidential Annex 2, information is also available in the public domain. Arkema (2006) indicates:

- 24% to 55% solutions are used mainly for water and effluent treatment; and
- 60% to 100% solutions are used for synthesis and manufacturing of hydrazine derivatives.

Solutions of hydrazine hydrate in a catalysed form are available from both known EU-based manufacturers of the substance (ICIS, 2009; Chemie.de, 2005). The catalyst is used to increase the reactivity of hydrazine hydrate in the solution.

3 INFORMATION ON MANUFACTURE, IMPORT, EXPORT AND RELEASES FROM MANUFACTURE

3.1 Production Process

3.1.1 The Olin Raschig Process

(Anhydrous) hydrazine is produced in the Olin Raschig process from sodium hypochlorite and ammonia, a process developed in 1907. This method relies on the reaction of chloramine with ammonia:

 $NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$

$$NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O$$

The optimal ratio of reactants is $33:1 \text{ NH}_3$:NaOCl and the only waste produced is brine, but this is still a significant issue on a plant scale. The major side reaction is the destruction of the hydrazine product by further reaction with chloramine (Matunas, 2004):

 $N_2H_4 + NH_2Cl \rightarrow 2 NH_4Cl + N_2$

The refining area has five steps: (a) ammonia removal, (b) NaCl concentration and removal, (c) hydrazine-water distillation to reach azeotropic concentration, (d) extractive distillation with aniline to break the azeotrope and (e) distillation to separate hydrazine from aniline. If hydrazine of very high purity is needed, freeze crystallisation is used to remove the supernatant fluid (Maxwell, 2004).

3.1.2 The Atofina-PCUK (Peroxide) Process

An improved synthesis process is the method known as Atofina-PCUK method, which is based on the Pechiney-Ugine-Kuhlmann process of a reaction of ammonia and hydrogen peroxide according to the following formula:

 $2 \text{ NH}_3 + \text{H}_2\text{O}_2 \xrightarrow{} \text{N}_2\text{H}_4 + 2 \text{ H}_2\text{O}$

In the Atofina-PCUK cycle, hydrazine is produced in several steps from acetone, ammonia, and hydrogen peroxide. The process is confirmed to currently be in use in the EU.

Unlike the Raschig process, this process does not produce salt. According to Matunas (2004), the Raschig process produces 4 tons NaCl/ton of hydrazine with a 60% yield (based on NH₃) and 125 kWh/ton hydrazine required. On the other hand, the Atofina-PCUK⁷ process gives no by-products, has a >80% yield (based on NH₃), and requires only 16 kWh/ton hydrazine.

3.1.3 The Bayer (Ketazine) Process

The Bayer (ketazine) process is based on the reaction of chloramine with ammonia in the presence of acetone at pH 12 to 14. NaOCl, acetone and a 20% aqueous solution of ammonia are fed into a reactor to make aqueous dimethyl ketazine solution. Excess ammonia and acetone are removed in a series of columns and are recycled into the reactor. The ketazine solution is distilled to make a hydrazine hydrate containing 64% hydrazine (i.e. 100% hydrazine hydrate) (Maxwell, 2004).

 $2 \text{ NH}_3 + \text{NaOCl} + 2 (\text{CH}_3)_2 \text{CO} \rightarrow (\text{CH}_3)_2 \text{C}=\text{N-N}=\text{C}(\text{CH}_3)_2 + 3 \text{ H}_2\text{O} + \text{NaCl}$

 $(CH_3)_2C=N-N=C(CH_3)_2+2H_2O \rightarrow N_2H_4+2(CH_3)_2CO$

PCUK stands for Produits Chimiques Ugine Kuhlmann, a French chemical manufacturer.

7

The process is confirmed to currently be in use in the EU.

3.1.4 The Hoffmann (Urea) Process

Another route of hydrazine synthesis involves oxidation of urea with sodium hypochlorite:

$$(H_2N)_2C=O + NaOCl + 2 NaOH \rightarrow N_2H_4 + H_2O + NaCl + Na_2CO_3$$

According to Maxwell (2004), this process was operated in 2001 but had found wider commercial use in the past. Compared with the standard Raschig process, it was considered to be the most economical for low production levels, but as plant sizes increased, it became obsolete. A Chinese-focused publication suggests that the urea process may still find use in China but notes that it would be eliminated due to considerations of environmental protection, product quality and production cost (China Chemical Reporter, 2007).

3.2 Production Sites

3.2.1 EU Production Sites

The market for anhydrous hydrazine in the EU is very low in comparison to the market for hydrazine hydrate. The information available from consultation indicates that there is currently no production of anhydrous hydrazine in the EU. Additional information explaining in more detail the supply chain is provided in Confidential Annex 2 to this report.

On the other hand, literature confirms that hydrazine hydrate is manufactured on two sites located in France and in Germany. Old information available on the ESIS database⁸ further suggests a production site in Spain. Consultation on the contrary confirmed that there has never been hydrazine hydrate production in Spain.

3.2.2 Non-EU Production Sites

Information from consultation suggests that anhydrous hydrazine is manufactured in countries such as the USA, Japan, China, and potentially Russia and India.

In relation to hydrazine hydrate, an article dated 2007 indicates that key global players are located, apart from France and Germany, in the USA and Japan (China Chemical Reporter, 2007). The same publication also mentions that around twenty (apparently less important at the time) Chinese companies were producing hydrazine hydrate in 2006.

It is uncertain whether production of the hydrate in the USA still takes place. A leading US company (well known for its activities in the field of anhydrous hydrazine for aerospace applications) may in fact represent a Korean manufacturer rather than manufacture the substance itself (Chang, 2007). In addition, the US-based manufacturing plant of a German manufacturer relocated to China a few years ago (Lanxess, 2005).

⁸ See here: <u>http://ecb.jrc.ec.europa.eu/esis-pgm/popup_hpvlpv.php?no=2061149&type=HPV</u>

Some additional information may be found in the Confidential Annex 2.

3.3 Production Volumes

3.3.1 Historical Information – Global Production

Back in 1981, global production of hydrazine was estimated to be in excess of 35,000 tonnes with major manufacturing capacities identified in the USA, Germany, France, Japan and the UK. More recent data estimate annual global production of hydrazine in 2004 at approximately 47,350 tonnes (Environment Canada & Health Canada, 2010). A market analysis in a Chinese-focused publication dated 2007 notes that the global production capacity for hydrazine hydrate had exceeded the level of 200,000 t/y (based on 100% hydrazine content). The capacity was divided near equally between Europe, Asia and America (35%, 34% and 30%, respectively), with only 1% in other regions (China Chemical Reporter, 2007). The same source suggests a worldwide market demand for hydrazine hydrate of 80,000-90,000 t/y. Assuming that Europe accounted for 35% of global demand (as for global capacity), demand within the EU in 2007 could have been 28,000-31,500 t/y.

3.3.2 Current EU Production

In relation to anhydrous hydrazine, current production is believed to be nil.

For hydrazine hydrate, detailed information has been obtained by the two key EU-based manufacturers. As the information is of a confidential nature, it is only presented in Confidential Annex 2 to this report. The combined production tonnage is in the 10,000-100,000 t/y range.

3.4 Imports into the EU

The EU demand for anhydrous hydrazine is covered by imports from non-EU countries such as China, USA, Japan and, potentially India and Russia. Estimates provided by consultees would indicate an imported volume in the 1-10 t/y range.

On the other hand, the consensus among industry experts is that imports of hydrazine hydrate into the EU must be low (in tonnage terms) in comparison to the tonnage of EU-based manufacture of the hydrated form. Some estimates on the volume of imports of hydrazine hydrate relative to the volume manufactured within the EU are available in Confidential Annex 2 to this report.

3.5 Future Trends

Some information on trends, both in relation to the possible future production of anhydrous hydrazine and its consumption in the EU are given in Confidential Annex 2, especially in relation to input made by **Company 15**.

Some information on past and possible future trends in the production of hydrazine hydrate has been made available by the two key EU-based manufacturers. These are presented in Confidential Annex 2 to this report. The available information does not suggest that significant changes are envisaged for the near future.

3.6 Information on Releases from Manufacture

3.6.1 Releases to the Environment from Manufacture

3.6.1.1 Information from Literature

Some rather old information is available for Germany. WHO (1987) reports old data from (the Federal Republic of) Germany according to which 0.06-0.08 kg of hydrazine were emitted to the air for every metric tonne produced, and an additional 0.02-0.03 kg were emitted for every metric tonne subjected to handling and further processing.

Outside the EU, the Japanese authorities confirm that, in 2001, hydrazine manufacturing plants in Japan released to air and water 434 kg and 7 tonnes, respectively. The authorities note that these were relatively low compared to releases from downstream applications (see **Table 5.2** later in the report) (CERI, 2007). That year, Japanese production of hydrazine hydrate was 15,373 tonnes.

3.6.1.2 Consultation Findings

Information has been provided by the two key EU-based manufacturers. As this is of a confidential nature, it is only available in Confidential Annex 3 to this report. It can be stated here that the information available confirms that some small releases of hydrazine to the atmosphere and the aquatic environment during manufacture are possible.

3.6.2 Releases to the Working Environment and Occupation Exposure during Manufacture

3.6.2.1 Information from Literature

Recent information on the occupational exposure associated with the production of hydrazine in the EU has not been identified. The information that follows thus relates to other jurisdictions.

IARC (1999) notes that exposure to hydrazine may indeed occur during manufacture. Some information on exposure of US workers to hydrazine during production was reported by the World Health Organization several years ago. This is reproduced in **Table 3.1**.

Table 3.1:OccuManufacture (hist)	pational Exposure to Ecorical data reported in 1	Hydrazine iı 986)	the	USA	– Pr	roduction	and	Derivative
Site	Approximate num	bers exposed			Measu	ured levels	s (mg	(m^3)

	Typical	Potential	Typical	Exceptional	
Production	100	800	<0.13	0.13-0.26*	
Production	No data	1,100	<0.35	<1.18	
Derivative manufacture	<25	No data	<0.13	Ca. 0.13	
Source: WHO (1987) * short-term samples during specific operations					

ATSDR (1997) notes that, since most hydrazine production processes involve closed systems, the potential for exposure is generally low. The greatest potential for exposure probably occurs during process stream sampling, with measured time-weighted average (TWA) concentrations ranging from 0.04 to 0.27 ppm (0.05 to 0.35 mg/m³) and occasionally reaching levels of up to 0.91 ppm (1.19 mg/m³)(based on Fajen & McCammon, 1988).

A cross-sectional survey was carried out on 172 male hydrazine hydrate-exposed workers (age 18-60, mean 39.6; exposure duration 0.50-34.17 years) and 125 male referent workers (age 19-58, mean 40.9) at five factories manufacturing hydrazine hydrate or hydrazine derivatives in Japan in the 1990s. Exposure concentrations were assessed by determining hydrazine in the breathing zones and urinary hydrazine+acetylhydrazine. The cumulative exposure level was assessed by multiplying the individuals' working durations at the job sites and the estimated past environmental levels at the job sites. No hydrazine was detected in either the breathing zones or the urine of the reference workers. The mean hydrazine concentration in the breathing zones, hydrazine+acetylhydrazine in urine, and cumulative exposure level were 0.0109 ppm⁹ (n.d.-0.2003), 0.8660 μ mol/g · Cr (n.d.-14.20)¹⁰, and 2.80 ppm-years (0.003-19) respectively (Nomiyama *et al*, 1998).

3.6.2.2 Consultation Findings

Information has been provided by the two key EU-based manufacturers. As this is of a confidential nature, it is only available in Confidential Annex 3 to this report. We can confirm that engineering and other protective measures are taken to prevent employees' exposure to the substance. The use of closed systems in the manufacture of the substance (in its hydrated form) should also be noted.

⁹ Equivalent to 0.014 mg/m³.

¹⁰ Cr stands for creatinine.

4 INFORMATION ON USES OF HYDRAZINE

4.1 Overview of Hydrazine Uses

4.1.1 **Possible Uses referred to in Literature**

Table 4.1 provides an overview of the range of applications for hydrazine that have been identified in literature. This is a collection of 'all' potential uses identified and includes applications for which hydrazine derivatives rather than hydrazine itself may be used. It should not be assumed that all these uses definitely are or have been relevant to the EU in the past.

Table 4.1: Examples of Search	of Possible Applications for Hydrazine and its Derivatives –	Results of Literature
Application area	Details/Notes	Example references
Hydrazine Hydrate	·	
Chemical synthesis	 Hydrazine is used to produce derivatives, which find wide uses. These include: blowing agents (such as azodicarbonamide for use in thermoplastics, elastomers (polystyrene, polypropylene, high and low density polyethylene, ABS, PVC)) bio-active intermediates for agrochemical and pharmaceutical products, also via triazoles and other hydrazine derivatives (salts) organic dyes (for textiles) photography developers spandex fibres/polyurethanes (acts as an extender) acrylics polymers (where the derivatives act as polymerisation initiators/catalysts or heat stabilisers) flame retardants lubricants solder fluxes for light metals (as hydrazine sulphate) synthesis of flocculants and coagulants 	Arkema (2006) Arkema (2010) Arkema (2005) Arch (2010i) Arch (2010j) NTP (undated) ILO (undated)
	Hydrazine may also be used in the synthesis of hydrobromic acid, iodine compounds (e.g. KIO ₃) and other organic compounds	
	 Hydrazine salts (solutions of dihydrazine sulphate 55% and hydrazine hydrochloride 35%) may also be used as: reducing agents: sulphuric acid de-NO_x oil-well treatment-stimulation agents anti-oxidants against corrosion in metallurgic processes 	
Water treatment agent	Used as an oxygen scavenger for industrial boilers, heating systems, high pressure steam generators for thermal and nuclear power plants	Arkema (2006)

Table 4.1: ExamplesSearch	of Possible Applications for Hydrazine and its Derivatives –	Results of Literature
Application area	Details/Notes	Example references
Effluent treatment	 Treatment of liquid and gas streams Scrubbing CO₂ and mercaptans from gaseous emissions 	Arkema (2006) Chemindustry.ru (undated)
Reducing agent for metallic deposition and recovery	 Metallisation of glass, plastics and metals (nickel, cobalt, iron, chromium) nickel and palladium electroless deposition Actired® process used mainly in gold mines for gold recovery from ores by activated carbon elution precious metal refining 	Arkema (2006) Arkema (2010b)
Explosives	In mixtures with ammonium nitrate (to give Astrolite)	Meyer <i>et al</i> (2007)
Purification agent	Purification of sulphuric acid for use in electronics Purification of hydrochloric acid	Arkema (2006)
Nuclear waste treatment	Extraction of plutonium and neptunium	Qiaoa <i>et al</i> (2009)
Semiconductors and electronics	Dissolution of materials for solar cell applications	Kalaugher, 2004
Other uses	 Making PCB holes conductive added into glass mass to remove dimness of glass automotive fuel cells can cleaning 	Scorecard (2010) Chemindustry.ru (undated) Atkins (2007) CERI (2007)
Anhydrous Hydrazine		I
Fuel for aerospace applications	 Propellant for space vehicles and satellites emergency power units for jet aircrafts emergency surfacing systems for submarines 	Matunas (2004) Arch (2010e)
Explosives	Used as a controlled explosive for fracturing underground rock formations in the secondary recovery of petroleum and natural gas	Arch (2010e)
Chemical synthesis	Used in the preparation of derivatives or in reactions which require hydrazine, but which cannot tolerate the water of an aqueous solution	Arch (2010e)
Electronics	No further detail available	Arch (2010e)

It appears that anhydrous hydrazine finds much less wide use compared to hydrazine hydrate. As will be discussed later in this Section, the main applications for anhydrous hydrazine is in aerospace and defence applications. The rest of this Section will focus on those applications that our research suggests they are currently of relevance to the EU industry.

4.1.2 Hydrazine Hydrate vs. Hydrazine Derivatives

It has to be clarified that often when a reference is made to hydrazine being used in a certain application, this may in fact relate to the use of a hydrazine derivative (hydrazine salt or other product of a reaction of hydrazine) in a particular use. For instance, literature may refer to the use of hydrazine in the manufacture of polymers; in reality, hydrazine may be used in a specific synthesis process to form a derivative that can act as a chemical blowing agent (CBA). This is in turn utilised in the production of polymers. Indeed, the very reactive nature of the hydrazine molecule makes hydrazine an extremely important reagent in the manufacture of a wide range of derivatives.

Table 4.2: Range of Hydrazine Hydrate and Derivatives and Relevant Applications					
Product category	CAS No	Example applications			
Hydrazine hydrate	L				
Hydrazine hydrate 24-35-55%	*	Mainly for water and effluent treatments			
Hydrazine hydrate 60-80-85-100%	*	Mainly for synthesis and derivatives manufacturing			
Liozan®	*	Activated hydrazine hydrate for boiler water treatment			
Hydrazine derivatives	L				
Hydrazine salts					
Dihydrazine sulphate 55%	13464-80-7	Synthesis intermediate, de-NO _x			
Hydrazine hydrochloride 35%	2644-70-4	Synthesis intermediate, oil-well treatment			
Acetylhydrazide	1068-57-1	Synthesis intermediate			
Triazoles					
1,2,4-Triazole	288-88-0	Synthesis intermediate for phytosanitary and pharmaceutical products			
Sodium salt of 1,2,4-triazole	41253-21-8	Synthesis intermediate for phytosanitary and pharmaceutical products			
3-Amino-1,2,4-triazole	61-82-5	Defoliation herbicide for vineyards and orchards			
4-Amino-1,2,4-triazole	584-13-4	Synthesis intermediate for pharmaceutical products			
Aminoguanidine bicarbonate (AGBC)	2582-30-1	Synthesis intermediate			
Azoics					
Azobis isobutyronitrile (AZDN)	78-67-1	Acrylic and vinyl polymerisation initiator, halogenations, low temperature blowing agent			
Azobis isovaleronitrile (AIVN)	13472-08-7	Acrylic and vinyl polymerisation initiator, halogenations			

Examples of the wide role of hydrazine derivatives are given in Table 4.2.

Product category	CAS No	Example applications
Azodicarbonamide (Azobul®)	123-77-3	Blowing agent
Source: Arkema (2005)	L	•
* this source incorrectly uses 302	2-01-2 as the C	AS Number; this is the CAS Number for the anhydrous

The manufacture of derivatives accounts for the significant majority of the overall amount of hydrazine hydrate consumed in the EU, as will be discussed in Section 4.2. Such uses of hydrazine have been characterised by industry stakeholders as **intermediate uses**, as defined under Article 3(15) of the REACH Regulation.

4.1.3 Information on Overall Use Patterns (Tonnage)

4.1.3.1 Information from Literature – Historical Information on Global Consumption

The global usage patterns for hydrazine have changed over the years, as shown in Table 4.3.

Table 4.3: Hydrazine Global Usage Patterns - 1960s to 2000s											
Year and Geographic Scope											
1964	USA	1977	World	1984	World	1995	World	2003	Japan	2007	World
Hydrazine		Hydrazine		Hydrazine		Hydrazine		Hydrazine		Hydrazine hydrate	
 Rocké prope 73% Interri in the synth agricu chem such a hydra blowi agent plastii pharn Is suc antitu isonia the antihy ve hydra and th fluxes hydra 	et Illant: nediate esis of iltural icals as maleic zine, ng s for cs, naceutica h as the bercular uzid and ypertensi lazine, ne solder s, zine ide and	 Synthesis of blowing agents: 34% Synthesis of agrochemical s: 32% Boiler water treatment: 19% Fuel: 5% 		 Synthesis of agrochemical s: 40% Synthesis of blowing agents: 33% Synthesis of polymerisatio n catalysts, and pharmaceutic al products: ? Boiler water treatment: 15% Chemical reducing agent in the metal-plating, metal recovery, and photographic industries Ignitor in 		 Synthesis of agrochemical s: 33% Water treatment: 26% Synthesis of blowing agents: 21% Rockets: 4.3% Others: 154% 		 Syntl blow agent Wate efflue treati can c 28% Syntl indus chem reduc deriv organ synth radic polyn initia azo comp epox harde modi agent 21% 	hesis of ing ts: 41% or and ent nent and leaning: hesis of strial ticals (as eer or ative for hic teesis, al nerisation tor for bounds, y resin ener, fibre fication ts, etc.):	 Syn pest 32% Syn blov agei Wat trea 20% Oth 	thesis of icides: thesis of wing nts: 33% ter tment: o ers: 15%

hydrazine chloride • Hydrazine hydrate used as a corrosion inhibitor in boiler water	 Smaller amounts are used as a rocket propellant and emergency fuel A very small amount of anhydrous hydrazine was used as a monopropella nt in space vehicles and 	 Synthesis of agrochemicals: 3% Synthesis of pharmaceutica 1s: 0.6% Other: 6.5% 						
Sources: WHO (1987): Schmidt & Wu	vehicles and satellites	mical Reporter (2007)						
Sources: WHO (1987); Schmidt & Wucherer (2004); CEKI (2007); China Chemical Reporter (2007)								

A key conclusion from this table is that, while use as a fuel (propellant) was very important in the 1960s, such use has declined and instead use of the hydrated form in synthesis and water treatment (as a corrosion inhibitor) has become more prominent.

In 2007, when the worldwide market demand for hydrazine hydrate was estimated at 80,000-90,000 t/y, the expectation was that demand would grow steadily, with demand in advanced countries declining while demand in developing countries, Asian countries in particular, growing rapidly (China Chemical Reporter, 2007).

4.1.3.2 Consultation Findings – Current Information on EU Consumption

Detailed information has been made available by key industry stakeholders and is available in Confidential Annex 2. In summary, the available information shows that uses of hydrazine hydrate in syntheses (synthesis of pharmaceuticals, agrochemicals and chemical blowing agents but also use as a monomer in the manufacture of waterborne polyurethanes), i.e. as an intermediate (as suggested by industry stakeholders and those companies registering the substance), use as a corrosion inhibitor and as a reducing agent for metals are the most important ones. Aggregated data would suggest the following (rough) breakdown of current uses of hydrazine in the EU:

- use in synthesis and as a monomer (pharmaceuticals, agrochemicals, chemical blowing agents, coatings, etc.): ca. 80%;
- corrosion inhibitors, metal reduction, refining of chemicals: ca. 20%;
- other (e.g. aerospace, defence and laboratory uses): very small percentage.

4.2 Use in Syntheses

4.2.1 Introduction

The following paragraphs provide a quick overview of the most important uses of hydrazine hydrate in synthesis that have been identified as relevant to the EU industry. On the assumption (proposed by industry) that these uses constitute intermediate uses, these should be exempted from authorisation under the REACH Regulation¹¹.

4.2.2 Pharmaceuticals and Agrochemicals

Hydrazine is a very reactive, bi-functional molecule, and therefore capable of entering into reactions leading to many types of biologically active compounds. Some of the ring systems based on hydrazine and frequently found in agricultural agents and pharmaceuticals include (Arch, 2010g; 2010h):



A useful overview of some of the active ingredients that may be manufactured with hydrazine or its derivatives is given by Novasep (2010). This suggests that these reagents give access to a variety of 1,2-diazatype heterocycles, thiosemicarbazides and azo compounds. Hydrazine hydrate and its derivatives are used in the manufacture of active ingredients for anti-cancer drugs, antidepressants, anti-fungus drugs, diuretics, anxiolytic, anti-arrhythmic, anti-allergic, anti-Parkinson, anti-haemorrhagic, anti-tuberculosis, antiviral, and anti-migraine drugs. In relation to agrochemicals, relevant preparations include herbicides, fungicides, insecticides, growth regulators, and systemic products (Arkema, 2005).

4.2.3 Chemical Blowing Agents

Chemical blowing agents (CBAs), also known as foaming agents, are added to polymers during processing to form minute gas cells throughout the product. The gas is liberated by a chemical change in the CBA (Arch, 2010i). Two hydrazine derivatives appear to be CBAs that find wide use, azodiisobutyronitrile (AIBM/AZDN) and azodicarbonamide. These can be used as low-temperature chemical blowing agents (80-120°C) for pressure-blown PVC and silicone rubber (Arkema, 2010b). End-applications include wind turbine blades, isolation panels, flotation devices, boat structures and seat foams, etc. (Arkema, 2010d). On the other hand, a US supplier of hydrazine suggests that azodicarbonamide is a CBA for medium temperature polymer

¹¹ As no specific and detailed information was available regarding those uses when writing this report, i twas not possible to check if those uses fulfill the definition as agreed by ECHA, the Commission and the Member States on the 4th May 2010 (http://guidance.echa.europa.eu/docs/guidance_document/clarificationintermediates_201005_en.pdf)

processing (160-220°C). Polymers using azo compounds include polystyrene, polypropylene, high and low-density polyethylene, ABS and PVC.

There are several other hydrazine-based chemical blowing agents such as benzene- and toluenesulphonylhydrazide, which are used in lower temperature applications (Arch, 2010i). Indirectly made from hydrazine, is the high-temperature blowing agent, 5-phenyltetrazole, which is used in several engineering plastics (Arch, 2010i).

4.2.4 Polymerisation Initiators and Catalysts

Hydrazine derivatives may be used in free radical polymerisation processes. Azo initiators derived from hydrazine hydrate are mainly used in polymerisation reactions to initiate or terminate the polymerisation process, or to reduce the residual monomer content. Their possible applications thus cover many fields (Arkema, 2010b):

- acrylic sheets, fibres, paints and coating resins;
- nonwoven textiles;
- grafted polyols; and
- co-polymerisation of vinyl compounds.

Relevant end-products may include wallpapers, gaskets, cables, sport footwear, tubing, wind turbine blades, isolation panels, flotation devices, seats foams, varnishes, paints, coatings, water treatment, synthetic glass, textile fabrics, etc. (Arkema, 2005).

Azo initiators such as AZDN are also used as catalysts for free radical halogenation or sulphochlorination (Arkema, 2010d).

4.2.5 Crosslinking in Urethanes and Acrylics

Hydrazine is bi-functional and very nucleophilic, allowing for a rapid reaction with isocyanates and acrylates. Therefore, hydrazine is added to various urethane mixtures to crosslink or chainextend the polymers. Crosslinking increases the strength and durability of the plastics allowing them to meet more rigorous demands (Arch, 2010j).

Apparently, both hydrazine hydrate and hydrazides can be used as crosslinking agents for polyurethane and rubber (Arkema, 2005). A substance used as a chain extender for polyurethanes with a N-N bond is adipic dihydrazide, $H_2NNH-C(O)-C_2H_4-C(O)-NHNH_2$ (Manea, 2003).

Use of hydrazine solutions for the production of coatings (presumably polyurethane ones) and other products has been confirmed by the Swedish Chemicals Agency (2010) as well by industry stakeholders.

4.2.6 Lubricants

Hydrazine-based sulphur compounds such as dimercaptothiadiazole (DMcT) have been reported as being the basis of a large number of lubricant additives (Arch, 2010j). Other hydrazine derivatives that may have found use as additives to lubricant formulations include
methylhydrazine, dimethylhydrazines, phenylhydrazine, etc. (Lubrizol, 1970). These uses have not been confirmed as relevant to the EU. It is also understood that polymers based on hydrazine may be used in lubricant formulations in the EU.

4.2.7 Nuclear Reactor Waste Treatment

All commercial nuclear waste reprocessing plants use the well-proven hydrometallurgical PUREX (plutonium uranium extraction) process. This involves dissolving the fuel elements in concentrated nitric acid. Chemical separation of uranium and plutonium is then undertaken by solvent extraction steps. The plutonium (Pu) and uranium (U) can be returned to the input side of the fuel cycle – the U to the conversion plant prior to re-enrichment and the Pu straight to mixed oxide (MOX) fuel fabrication. Modified versions of PUREX are also available such as UREX (it does not involve the isolation of a Pu stream) (World Nuclear Association, 2010b).

All processes in which U is separated from Pu take advantage of the fact that Pu valences are easily increased or decreased under conditions in which U remains as the uranyl (VI) ion. In all PUREX solvent extraction processes, the U(VI) and the Pu(IV) are co-extracted into a tributyl phosphate (TBP) solvent. This separates both the U and the Pu from most of the radioactive fission products that remain in the aqueous stream and that are sent to waste. To separate Pu from the solvent (and the U), a chemical reductant is added to reduce the Pu to the (III) valence. The Pu(III) has only a very weak affinity for the TBP, so the Pu is extracted into the aqueous phase (US Department of Energy, 1999).

Mixtures of U(IV)/hydrazine can be used in PUREX operations where small concentrations (up to 1%) of U in the Pu product are not a concern. The most beneficial attributes of uranoushydrazine mixtures are that they contribute no solids to waste, and they give rapid Pu reduction. Hydrazine is often called a holding reductant in that it eliminates those elements or components that would react with the primary reductant such as hydroxylamine nitrate, according to the following reaction (US Department of Energy, 1999):

$$N_2H_4 + 2 HNO_2 \rightarrow 3 H_2O + N_2 + N_2O$$

The French reprocessing plant at La Hague has used hydroxylammonium nitrate for reductive stripping of Pu. The chemical is received at 1.9M and then diluted and mixed with nitric acid and hydrazine for use in the process (US Department of Energy, 1999). The World Nuclear Association (2010) suggests that the French plant in La Hague processes light water reactor fuel (LWR) with a capacity of 1,700 t/y. The UK Thermal Oxide Reprocessing Plant (THORP) plant in Sellafield also has a capacity of 900 for LWR fuel. In addition, the UK Magnox plant, also in Sellafield, has a capacity for 1,500 t/y for the processing of other nuclear fuels.

Some information of a confidential nature on this use that has been collected during consultation is provided in Confidential Annex 2.

4.3 Use in Water Treatment

4.3.1 Description of Use

4.3.1.1 Background (including Information from Literature)

Steam being 'pure' water dissolves other materials into it very easily and it is these other materials that cause problems requiring treatment; such materials include metals from the system, oxygen, carbon dioxide and others. The major problems that may arise from the presence of these materials are scale, corrosion, boiler water carryover, and sludge deposition (Accepta, 2010).

It is believed that in several industry sectors the removal of dissolved oxygen from process (boiler) water is important, but among them, power generation should be the one where such removal plays an exceedingly important role. Oxygen corrosion occurs through an electrolytic process using the plant system's metal as a current path and the process water phase as an electrolyte. Oxidation takes place at the anode where a pit is formed. At the cathodic surface, oxygen reacts with hydrogen and depolarises the surface, permitting more iron to dissolve at the anode, gradually creating a pit. It is therefore important to remove oxygen from the system (Eurelectric, 2010).

Hence, the control of corrosion of power plant components is critical to maintain the plant's performance, availability and life, i.e. getting the most from capital investment in the plant. Such corrosion can take place throughout the entire feed and boiler system (Eurelectric, 2010).

Removal of oxygen is typically a two-stage process (Eurelectric, 2010):

- Stage 1: mechanical, meaning using vacuum (degassing the cold make-up water in the condenser) and thermal deaeration (heating the water and spraying into a deaerator to maximise surface area and subsequent degassing). Under steady operating conditions, a well-maintained plant can achieve oxygen levels of $<10\mu$ g/kg in the feedwater. These small traces of oxygen, however, can still influence corrosion in the plant systems. More significantly, due to commercial considerations, most generating units do not maintain steady operating conditions and consequently experience deviations in oxygen levels (increased make-up, disturbed conditions in the deaerator, increased air intake over the sections that operate under vacuum); and
- **Stage 2**: to support the mechanical means of oxygen removal, it is necessary to add a chemical oxygen scavenger to remove trace residuals or mitigate impacts during times of idleness.

As powerful reductive agents, hydrazine hydrate and its salts can be used as oxygen scavengers for boiler water and feedwater treatment. Hydrazine hydrate may be used either in the form of a simple solution or in its catalysed form (Arkema, 2005). Hydrazine reduces this corrosion in three ways (ABB, 2005):

- **Direct reaction**: hydrazine reacts with oxygen to form nitrogen and water:

$$N_2H_4 + O_2 \rightarrow N_2 + 2 H_2O$$

- **Decomposition**: hydrazine breaks down into ammonia at high temperature (>200°C) and pressure; this increases the pH of the water, thus reducing the risk of acidic corrosion:

$$3 N_2H_4 \rightarrow 4 NH_3 + N_2$$

Passivation: hydrazine reacts with any soft haematic (Fe_2O_3) layers on boiler tubes and changes them to a much harder layer of magnetite (Fe_3O_4):

$$N_2H_4 + 6 Fe_2O_3 \rightarrow 4 Fe_3O_4 + 2 H_2O + N_2$$

The magnetite layer helps to protect the boiler tubes from damage in the event of dissolved oxygen surges and gives a certain amount of protection against dissolved salts. However, unless an excess of hydrazine over and above the amount needed to scavenge the oxygen is present, this layer reverts to haematite and the protection is then lost (ABB, 2005).

Hydrazine hydrate solutions can be used both during the operation of boiler systems but also for the maintenance of boilers during maintenance/shutdown periods, also known as 'wet lay-up'. While dry lay-up of boilers may be desirable for long-term storage, properly carried out wet lay-up can provide the needed protection during lay-ups such as those which may occur during low production periods, plant breakdowns and during regular maintenance periods. A boiler system that will be needed on very short notice can be placed in wet lay-up. The primary purpose of wet lay-up is to keep a boiler clean and inhibit corrosion in 'idle' or 'stand-by' boiler equipment. This protection is also required either during pre-clean-up or pre-operational periods for greater convenience (Arch, 2002):

- by aiding in the formation of protective thin films; and
- by sustaining absorbed barrier layers.

Hydrazine is convenient for wet lay-up because it is a volatile liquid and does not increase the dissolved solids in the boiler drum. Neither hydrazine, nor its decomposition products, or its reaction products are acidic. In addition, wet lay-up with hydrazine penetrates all crevices and loose scale and use of hydrazine in wet lay-up requires no special treatments to remove excesses at time of start-up (Arch, 2002).

4.3.1.2 Consultation Findings

The most important application of hydrazine as a corrosion inhibitor is in nuclear and thermal power stations and our discussion here largely focus on the power generation sector (see **Box 4.1** for a description of the processes in power plants and the importance of corrosion control). However, hydrazine hydrate solutions find uses in other types of plants, as will be discussed later in this Section.

Box 4.1: Operations of Nuclear and Fossil-fired Power Plants

Company 26 has provided an overview of the operation of nuclear and thermal power plants. The nuclear plant process can be simplified into two circuits, a "primary" and a "secondary" with as an interface between the two, the steam generator:

- the primary circuit function is to create thermal energy in the form of heated, pressurised water. It consists in a nuclear reactor, pipes and pumps;
- the secondary circuit function is to transform this thermal energy into electricity. It consists of an electrical generator, a turbine and heat exchangers; and
- a steam generator transforms the hot pressurised water from the primary circuit into dry steam for the secondary circuit, using exchanger tubes. The walls of these tubes constitute the physical barrier between the radioactive primary circuit and the secondary.

The process of a thermal (fossil-fired) power plant is similar except that the nuclear reactor is replaced by coal/oil burners and that there is no need to separate the primary/secondary units since there are no radioactive fluids to manage. This requirement for containment is crucial for a nuclear plant: it is the guarantee that materials or active fluids cannot escape. This requirement is ensured in particular by an efficient chemical control of the primary and secondary fluids in order, in particular, to maintain the complete integrity if the steam generator tubes, the physical barrier between the nuclear and classical parts of the plant.

Below information collected from consultation is presented, first by company and then by national Competent Authority.

Companies: **Company 26** has described how hydrazine is used in a number of nuclear and fossil-fired power plants owned by the company. This information is summarised in **Table 4.4**.

Table 4.4: Description of Hydrazine Hydrate Use as a Corrosion Inhibitor in Power Plants – Company 26						
Application of hydrazine hydrate	Operational status	Description of action	Transformation of hydrazine			
Nuclear plants						
Reduction of oxygen and pH regulation by hydrazine hydrate: corrosion inhibitor for equipment of a nuclear power plant	Plant in operation	Controlling the oxygen concentration by chemical conditioning of water in the closed circuit (closed) primary in their commissioning, and maintaining a reducing environment within the secondary circuit, to prevent corrosion of equipment and thus preserve the nuclear safety and generation functions	Substance thermally decomposed into ammonia (contribution to the maintenance of specified pH and nitrogen)			

Application of hydrazine hydrate	Operational status	Description of action	Transformation of hydrazine
Reduction of oxygen by hydrazine hydrate: corrosion inhibitor for steam generators of a nuclear power plant	Plant shut down for maintenance (in outages)	Controlling the oxygen concentration by chemical conditioning of water from the secondary steam generator circuits, and other exchangers if necessary, of nuclear installations, to prevent corrosion – including the physical barrier between the primary (radiologically active circuit) and the secondary circuit – and thus preserve the nuclear safety and generation functions	No transformation – hydrazine is a reducer of oxygen
Fossil-fired plants			
Reduction of oxygen and pH control by hydrazine hydrate: corrosion inhibitor for equipment of a conventional power plant	Plant in operation	Controlling the oxygen content by chemical conditioning of water from the main boiler and heat exchangers and preventing corrosion of equipment and thereby preserving the generation functions	Yes, substance thermally decomposed into ammonia and nitrogen
Reduction of oxygen by hydrazine hydrate: corrosion inhibitor for the boilers of a conventional power plant	Plant shut- down for maintenance	Controlling the oxygen content by chemical conditioning of water from the main boilers and thereby preserve the generation functions	No transformation – hydrazine is a reducer of oxygen

Another company operating power plants, **Company 32**, has further confirmed its use of hydrazine hydrate (55% solutions are purchased) for oxygen scavenging in nuclear power plants. Hydrazine is stored and dosed into the boiler feedwater to remove oxygen and so maintain reducing conditions in the evaporator and superheater regions. In AGR (advanced gascooled) boilers and PWR (pressurised water reactor) steam generators, hydrazine serves to ensure that oxygen does not reach austenitic sections, where oxygen might otherwise promote stress corrosion cracking during on-load operation. The feedwater oxygen concentration specified for AGR boiler inlet, during on-load operation is typically ~ 25-70 μ g/kg, with hydrazine being dosed at ~ 1.8 x [O₂].

Similarly, hydrazine is also employed in several low temperature applications during off-load operation (e.g. decay heat removal and wet storage (lay-up) applications, etc.). Here, the rate of oxygen removal is lower than that at full-power conditions because of the lower temperature and pressure. In this case, the feedwater oxygen concentration for AGR boiler inlet is

maintained at less than ~ 30 μ g/kg, where hydrazine is dosed at ~ 1.5 x [O₂]. Hydrazine is therefore preferentially utilised for its versatility when varying the power in the reactor¹².

Another energy company, **Company 22** confirmed that it uses hydrazine in power plants but also in water steam circulation for district heating and cooling. The concentration of hydrazine hydrate in the solution is 15% and the presence of hydrazine ranges from very low in the boiler water up to 150 μ g/kg in the water user for district heating and cooling¹³.

Company 52 is also an operator of power plants. In 2009, the company used 50 tonnes of a 5% hydrazine hydrate solution (containing an equivalent 1.6 tonnes of anhydrous hydrazine).

Company 57, a contractor for the nuclear power industry used in 2009 hydrazine hydrate solutions containing 3 kg of hydrazine (expressed as anhydrous form) for oxygen reduction and corrosion inhibitor in nuclear power plant circuits.

Finally, **Company 44**, also a contractor for the nuclear power industry, has advised that it uses hydrazine hydrate solutions for the chemical cleaning of steam generator rather than for boiler feedwater treatment. The accumulation of deposits in the secondary side of PWR steam generators increases the potential of accelerated tube degradation. As the deposits harden and form crevices, they can cause conditions that can lead to tube corrosion or operational concerns. There are a number of different mechanical and chemical cleaning methods available to remove steam generator deposits. One of these methods, steam generator chemical cleaning, involves the introduction of chemicals to dissolve deposits. Steam generator chemical cleaning is best suited of plants with significant deposit accumulation (an estimated 3,000 pounds – 1,360 kg – or more per steam generator). The company uses purchases 55% hydrazine hydrate solutions, which it dilutes to a 0.1-2% concentration before use.

Competent Authorities: information has been received from the Cypriot Department of Labour Inspection (2010). It appears that catalysed solutions of hydrazine hydrate with a concentration of 55% are imported from another EU country for use in two power stations on the island.

The German Federal Institute for Occupational Safety and Health (2010) indicated that 15% hydrazine hydrate solutions are used in the country as an oxygen scavenger and a corrosion inhibitor in water and steam systems (e.g. boilers).

Use of hydrazine solutions as corrosion inhibitors has been confirmed by the Swedish Chemicals Agency (2010).

Finally, the UK Health and Safety Executive also confirms the use of hydrazine hydrate as an oxygen scavenger in boiler feedwater in power stations (HSE, 2006). The only other use at the time was in syntheses.

¹² Hydrazine (50ppb) is also utilised as a laboratory reagent to formulate standards for UV/Vis Calibration purposes.

¹³ We have been advised that important factors which will influence the required concentration of hydrazine hydrate in solutions used for water treatment are: the quality of the boiler water, the type of boiler equipment, other treatment processes which are used in combination with hydrazine dosage, the construction material for the boiler, guidelines of the engineering companies (process developers), and process safety demands.

4.3.2 Locations and Quantities Used

4.3.2.1 Industry Sectors Potentially using Hydrazine Hydrate

It is currently uncertain in which industry sectors, apart from power generation, hydrazine is currently used as a corrosion inhibitor in the EU. Some suggestions have been made by experts in the industry: a representative of **Company 23** has advised that typical industries in which hydrazine hydrate oxygen scavengers could be used include all steam-using industries, such as the chemical industry, the refining and petrochemical industry, the pulp and paper industry, the steel industry, the food industry etc. It can be assumed however that, in the food industry, the application of hydrazine must be very limited or not existing, but in the other sectors boiler treatment with hydrazine can conceivably be found. Indeed, a key company in the hydrazine hydrate supply chain has confirmed the use of the substance by steel plants and chemical products manufacturers.

Company 23 also believes that while power generation plants have very strict conditions for handling hydrazine hydrate solutions, in other boiler systems the conditions may often be less strict. Especially smaller boiler systems will not use closed dosing systems like the ones applied in power generation plants.

A Canadian Government publication confirms that hydrazine may be used (and released) in the boiler systems of industrial plants other than power generation units. In principle, these systems use much less hydrazine than that used to counter oxidation in cooling systems of boilers, i.e. power plants (Environment Canada & Health Canada, 2010).

4.3.2.2 Locations of Power Generation Plants

As of October 1, 2010 there is a total of 143 nuclear power plant units with an installed electric net capacity of 131 GWe in operation in the EU and 6 units with 5.8 GWe were under construction in four countries (European Nuclear Society, 2010). The World Nuclear Association (2010) provides a list of EU countries where electricity may be generated through nuclear power plants; fifteen Member States produce between 4% and 80% of their electricity through nuclear power plants. Details on the number of fossil-fired power plants are not available; however, Eurelectric (2010b) suggests that, in 2009, electricity generation capacity from conventional (fossil-fired) plants in EU-27 was around 475 GW (while the capacity of nuclear plants was 133 GW). It is therefore reasonable to assume that the number of fossil-fired power plants in the EU is larger than the number of nuclear power plants.

4.3.2.3 Locations of Other Potential Users

A Swedish company, **Company 19**, which claims to be a world leader in the field of water treatment for boilers in the pulp/paper industry but also in power plants, has commented that hydrazine is still commonly used in eastern Europe and is still in use in parts of Southern Europe (Portugal and Spain). Conversely, the use of the substance is practically banned in Scandinavia; it is the handling of hydrazine that is not allowed, due to its classification, although purchase and exporting is not prohibited. The company has also not used hydrazine in France or the Benelux countries in the last two years.

Some additional information has also been provided by the Confederation of European Paper Industries (2010). The Confederation enquired among its members on whether the substance is used in water treatment applications. The feedback received would suggest that hydrazine is not used in wastewater treatment as mentioned by the literature, although it may have been used in the past in boiler water preparation and the corrosion protection of boilers. Hydrazine is no longer used as it is known to be carcinogenic and some Confederation members mentioned that it was phased out in the late 1980s when it was replaced by DEHA or carbohydrazide which have a more favourable hazard profile. The assumption that hydrazine is unlikely to be used in the EU paper/pulp sector has been corroborated by the accounts of two individual companies, **Company 10** and **Company 11**. In **Company 11**'s country, hydrazine was replaced around 1990 due to its carcinogenicity classification.

4.3.2.4 Quantities Used

Some information on the sales of hydrazine hydrate for use as a corrosion inhibitor is available from the two manufacturers of the substance and is presented in Confidential Annex 2. In addition, **Company 26** has also provided information on its use of hydrazine in nuclear and fossil-fired power plants; this is also provided in the Confidential Annex.

Some additional information that can be presented here is available from the following companies/organisations:

- the energy-producing **Company 22** advised that it uses <10 t/y of a 15% hydrazine hydrate solution per year (this is equivalent to <1 t/y anhydrous hydrazine);
- **Company 57** uses solutions containing only a few kilograms of hydrazine for the treatment of boiler feedwater in nuclear power stations;
- **Company 44**, a contractor for the nuclear power industry, uses between 100-1,000 t/y of solutions for solids removal but, due to the very dilute solutions used, the actual consumption of hydrazine hydrate is in the 0.1-10 t/y range;
- according to the Cypriot Department of Labour Inspection (2010) a total of 8 tonnes of a 55% solution (equivalent to 2.8 tonnes of anhydrous hydrazine) was imported into the island and consumed in 2009 in power generation (2 plants);
- power plant operator **Company 32** purchases ca. 75 t/y of hydrazine hydrate 55% (equivalent to 26.4 tonnes of anhydrous hydrazine) across eight operating power stations;
- the material that is ordered by the customer of supplier **Company 13** is used up in the process and is usually per treatment; treatments are normally only 2-3 a year. Depending on boiler size, the amount of hydrazine solution used could be up to 200 kg per treatment and the concentration of hydrazine hydrate in the solution supplied has a concentration of 35%; and
- **Company 19** also uses up to 200 kg per application but prefers to use a 15% catalysed solution. It should be noted that contrary to almost all other consultees, this company uses hydrazine not only in power stations but also installations such as paper and pulp plants.

It should be understood that dosage is controlled through measurements, thus consumption follows the amount of oxygen in feedwater and condensates.

4.3.3 Recent and Future Trends

Information from some key players is provided in Confidential Annex 2. Some information that can be provided here is summarised below.

Table 4.5:Pase(Corrosion Pro	t and Futu tection) – S	re Trends Selected Co	in Consumption of Hydrazine Hydrate for Water Treatment mpanies
Company responding	Last 5 yrs trend	Future trends	Details
Company 22	Down >25%	Stable	The decreasing trend in hydrazine use has been partly due to following more precise process conditions, which has made it possible to decrease the use of hydrazine hydrate. In addition, the variation in the annual usage of power plants may also affect hydrazine use. The target of the company is to maintain or even decrease the use of hydrazine hydrate. However, the ageing of plants, the quality of water and the length of operation shutdowns are expected to sustain to an extent the demand for hydrazine
Company 32		Stable	Expected to remain essentially stable over the coming years as its consumption relates to the consistent rate of usage at the company's nuclear power stations to achieve the company's internal governance requirements
Company 13	Varied		The quantities sold between 2008 and 2010 were below 1 tonne per year and fluctuated significantly; usage depends on power station maintenance schedule hence consumption volumes can differ considerably from one year to another
Company 44		Stable	Only recently started using hydrazine hydrate as a contractor for nuclear power plant and expects consumption to remain largely stable in the foreseeable future
Company 52	Stable	Stable	Optimised consumption, proportional to operations, hence no real changes are envisaged
Company 57	Stable		No details given
Source: Consul	tation		

It is worth noting the input of **Company 8**, a boiler manufacturer. The company suggested that, whilst use of hydrazine hydrate was the normal practice in the past, research has shown that its use is not without problems. The company indicated that key European contractors and operators of utility power plants have stopped continuous hydrazine injection in water cycle for new projects. This may not be the case for existing plants. Some additional detail is provided in Section 6.1.1.

Information from certain consultees (**Company 19**, **Company 8** but also members of the Confederation of European Paper Industries) suggests that the use of hydrazine may be in decline. Several companies have explored alternatives and whilst power station operators generally appear to have been unable to identify alternatives that could meet their requirements, other companies may have opted for alternatives (for example, see the testimony of UK Company 9 which argues that hydrazine has largely been replaced in high-pressure boilers by alternatives such as carbohydrazide, diethyl hydroxylamine (DEHA) and isoascorbic acid, as

well as the information provided in Section A2.4.1 of Confidential Annex 2 and A3.3.2 of Confidential Annex 3 on the patterns of use of hydrazine hydrate in smaller and newer installations).

4.3.4 Structure of Supply Chain

End-users such as power plants tend to purchase hydrazine hydrate solutions either from the manufacturers or distributors. It is also possible that the removal of oxygen may be undertaken by contractors, companies that specialise in the treatment of water.

4.4 Use as Reducing Agent for Metals

4.4.1 **Description of Use**

4.4.1.1 Information from Literature

Electroless Plating

Electroless plating (also known as autocatalytic plating) is a selective deposition plating process in which metal ions are reduced to a metallic coating by a reducing agent in solution. Plating takes place only on suitable catalytic surfaces, which include substrates of the same metal being plated, hence the term 'autocatalysis' (Seshan, 2001). Depending on the nature of the metal to be deposited, the reducing agent employed may vary. Typical reducing agents include sodium hypophosphite, sodium borohydride, hydrazine and dimethylamine borane (Jerry Barker Consultants, 2010).

Literature sources refer to the use of hydrazine in **electroless nickel deposits** where it is able to provide pure metal coatings, as opposed to the use of sodium hypophosphite (NaH₂PO₂.6H₂O) which results in a phosphorus content of the final coating of 3-15 wt% (Sidorenko & Kukin, 1977; Mittal, 1998; and Bicak *et al*, 2002).

Literature also indicates that hydrazine may be used in **electroless platinum and palladium deposits**. Reducing agents used for electroless plating of palladium include hydrazine, hypophosphite, amine borane, and formaldehyde. Hydrazine baths apparently suffer from a serious drawback: the plating rate decreases rapidly during bath operation to a much greater degree than expected from the depletion of palladium in the bath, because of the catalytic decomposition of hydrazine itself. Hypophosphite baths do not have this problem and have been investigated more extensively (Okinaka & Wolowodiuk, undated). Electroless platinum has been plated using hydrazine or borohydride as the reducing agent. However, the operation of those processes appears to be more difficult than that for electroless palladium (Okinaka & Wolowodiuk, undated). Ruthenium and rhodium coatings may also be deposited with hydrazine acting as the reducing agent (Okinaka & Wolowodiuk, undated; Vakelis, undated).

Electroless silver and gold deposits are also possible. Electroless silver plating solutions have been developed using cyanide Ag(I) complex and aminoboranes or hydrazine as reducers (Vakelis, undated). The oldest application of the process is the silvering of glass and plastics for producing mirrors using silver nitrate solutions and one of various reducing agents, hydrazine among them (Seshan, 2001). Thin gold coatings may be deposited on plastics by an aerosol

spray method: gold complexes with amines are employed with hydrazine as a reducer, and a relatively thick coat may be obtained (Vakelis, undated).

Recovery of Precious Metals

Literature suggests that hydrazine hydrate may be used in the *aqua regia* gold refining process. This process is probably the most widely used at the small-medium scale by jewellers and refineries alike and can produce gold of up to 99.99% purity. It is based on the ability of *aqua regia* (a mixture of hydrochloric and nitric acids in a 4.5:1 ratio) to dissolve gold. Thus, the scrap gold is dissolved in the acid mixture to form soluble gold chloride. Silver chloride is precipitated and filtered off. The gold is selectively precipitated from solution by a reducing agent and filtered off, washed, dried and the resultant powder melted to a solid button or ingot. Hydrazine can be one of those reducing agents (Corti, 2002).

Platinum may also be recovered from jewellery waste using hydrazine. Kady Mbaya (2004) recounts how platinum with a purity of 99% was recovered by precipitation with ammonium chloride (NH₄Cl) as ammonium hexachloroplatinate complex (NH₄)₂PtCl₆ and converted to black platinum powder using hydrazine. The process can be described by the following chemical reactions (Kady Mbaya, 2004):

8 HCl _(aq) + 2 HNO_{3 (aq)} + Pt _(s)
$$\rightarrow$$
 H₂PtCl_{6 (aq)} + 4 H₂O _(aq) + 2 NOCl _(g)

$$H_2PtCl_{6 (aq)} + 2 NH_4Cl_{(aq)} \rightarrow (NH_4)_2[PtCl_6]_{(aq)} + 2 HCl_{(aq)}$$

$$(NH_4)_2 PtCl_{6 (aq)} + N_2H_{4 (l)} + 6 NaOH_{(s)} \rightarrow Pt_{(s)} + 6 NaCl_{(aq)} + 2 NH_{3 (g)} + N_{2 (g)} + 6 H_2O_{(aq)}$$

Apart from jewellery, noble metals such as platinum group metals may also be recovered from waste using hydrazine hydrate – for instance, in the electronics industry. Frankham & Kauppinen (2010) note that platinum group metals (PGMs) can be recovered by reduction using reagents such as hydrazine or sodium borohydride – although hydrazine is reportedly becoming less acceptable for use in industry due to its hazardous properties and handling issues.

4.4.1.2 Consultation Findings

Electroplating

According to Lloret (2010), hydrazine can be used in electroplating baths based on chromium (III) at a dosage of 120 g hydrazine sulphate per litre. Hydrazine plays three distinct roles:

- the bathroom uses graphite anodes. Anodic oxygen evolution during electrolysis causes erosion of the anodes. The reaction of hydrazine with oxygen causes the formation of nitrogen near the anode, preventing erosion;
- during the electroplating, a secondary reaction takes place at the anode: the oxidation of chromium (III) to chromium (VI). Chromium (VI) acts as a potent contaminant of the bath. The presence of a reducing agent such as hydrazine again reduces chromium (VI)

to chromium (III). This is achieved by limiting the presence of chromium (VI) to 0-2 mg/L; and

• hydrazine can improve the corrosion resistance of chrome plating due to the reduction of porosity.

The bath of chromium (III) includes this species as chromium (III) sulphate or chromium (III) chloride. Once chromium (III) is released in the solution, the complexing agents in the bath (e.g. formic acid or its salts) stabilise it. The bath also contains boric acid which acts as a buffer to stabilise the pH in the correct range (between 2 and 3). Under these conditions, hydrazine would be unstable. It is therefore added in the form of a compatible salt, sulphate, sulphite or chloride (Lloret, 2010b)¹⁴.

However, consultation with **Company 1** suggests that whilst hydrazine salts have been referenced in patent literature as relevant to trivalent chromium baths, these are not really used in the EU as described above. Instead, some limited actual use takes place in the area of hexavalent chromium: hydrazine hydrate (rather than one of its salts) is used as a reducing agent in the process following the etching of plastic surfaces (which involves chromic acid). Typical concentrations of the hydrate would be 1-5% in the concentrate sold to the plater, with a final 0.01 to 0.05% in the plating bath.

The company notes that efforts are being made to phase hydrazine out because of its toxicity. Hydrazine-free products (hydroxylammonium compounds and hydroxy acids) are available but it is claimed that there is some customer resistance to change.

Finally, **Company 54**, a supplier of metal surface treatment solutions confirmed that in the past hydrazine hydrate solutions (of a concentration of a few g/L) were sold for addition to gold plating bath formulations. The function of hydrazine was mainly to enable the use of higher current densities without having irregular deposit growth in the areas of the part more exposed to anodic current flow. The relevant product is no longer sold by the company.

Electroless Plating

Lloret (2010) has provided an overview of potential uses of hydrazine in the electroless plating. This is presented in **Table 4.6**.

Company 5 advised that hydrazine has largely been replaced by hypophosphite or boranes and it may be used for special applications only, but not really for plating on plastics.

Experts in the sector (from **Company 2, Company 5** and **Company 6**) confirm that hydrazine has been used as a reductant in electroless nickel, platinum and palladium processes. For nickel plating, its advantage is that it produces a pure nickel deposit as opposed to the nickel-phosphorus (NiP) alloys produced by solutions using hypophosphite or nickel-boron (NiB) alloys produced when using boranes as a reductant. Pure nickel is soft, malleable and ductile and has a high melting point. NiP and NiB deposits are much harder as plated and are not malleable or ductile.

¹⁴ A basic rule of development of galvanic treatment baths is that the additives are incorporated in a manner consistent with the rest of the components, avoiding the introduction of undesirable species (contaminants). Thus, in alkaline baths (cyanide based baths, amine baths, etc.) hydrazine is incorporated as such rather than as a salt – the addition of hydrazine salt (sulphate, chloride, etc.) generally aims to achieve greater stability given that hydrazine alone is more unstable; however, the presence of sulphates, chlorides, etc. pollutants can be undesirable (Lloret, 2010b).

There are some applications for pure nickel, which are limited by the poor throwing power of electrolytic techniques - these may be overcome by electroless deposition using hydrazine. However, it is a much more expensive and hazardous route. Therefore, so far the use of hydrazine has been driven by research rather than by application, and commercial uses of such techniques are likely to be limited (some limited use in universities or aerospace research establishments has been suggested).

Table 4.6: Potential Uses of Hydrazine (and its Salts) in Electroless Metal Plating				
Type of bath	Typical hydrazine dosage	Details		
Plating of precious metals				
Deposition of gold and gold alloys for electronic applications	8 g/L hydrazine	Gold over nickel coatings from baths with cyanide		
Deposition of electroless gold (compatibility with the positive photoresists)	25 g/L hydrazine chloride	Non-cyanide baths (sulphite-based gold (I))		
Deposition of palladium for electronic applications	0.3 g/L hydrazine	Allows for sequences of stable layers for contacts in conductors operating at high temperatures. Used to give gold sub-layers to prevent diffusion of substrates of copper or silver through gold*. Palladium-amine bath		
Deposition of platinum for electronic applications	1 g/L hydrazine	Hexahydroxoplatinate baths		
Deposition of silver coatings for glass or ceramics as insulators (spray method)	4.5 g/L hydrazine sulphate	Bath of silver nitrate in ammoniacal solution		
Plating of basic metals				
Deposition of nickel films containing pure nickel (99%) for semi-conductors	4.5 g/L hydrazine sulphate	With sodium tartrate as a complexing agent		
Source: Lloret (2010; 2010b) * When a copper or silver alloy (base diffusion effect that can reach the sury These spots are the products of alloys will change the conductive properties the thinner the layer of gold. To avoid barrier to diffusion. The most common	alloy or coating) face and cause sta or "intermetallic. of the gold surfac d this diffusion eff n barrier layers an	lies underneath a coat of gold, there is a ins that are confused with corrosion products. s" of gold and copper or gold and silver, which e. The phenomenon of diffusion is much faster ect, intermediate coatings are used to act as a re nickel or palladium. In the present case,		

palladium is applied in electronics since in electronics it is important the presence of precious metals as a final topcoat. If due to usage, there was a failure or defect, with the release of gold, the underlying palladium would guarantee that the system would still work smoothly

Recovery of Precious Metals

Company 24, Company 29 and Company 30 have provided information on the use of hydrazine as a reducing agent in the production of precious metals, including precious metals

catalysts. Due to the commercially sensitive nature of the information provided, this is presented in Confidential Annex 2.

Company 20 uses hydrazine hydrate (solutions of high concentration) in the production of AgCdO, $AgSnO_2$ and Ag powders by chemical reaction. These powders are subsequently used for die compaction or extrusion of electrical contacts (electrical contacts are used in relays, contactors, circuit breakers, etc.).

Two more companies have confirmed some minor use in this field:

- a supplier of precious metals (**Company 12**) has confirmed it is using a very small quantity of the substance (<1 litre per year) in the refining of high PGM-containing material. The company is currently looking for alternatives to hydrazine; and
- **Company 31** has also indicated that it uses <1 litre of hydrazine hydrate each year. The company precipitates gold from jewellery scraps. The amounts of gold are always less than 5 g to 10 g for each reduction, and this takes place four or five times a year. This gold is refined, after washing and drying, with the rest of the company's scraps (it is diluted 5: 50,000 in the refining batch). The hydrazine hydrate solution has a concentration of 60%. The company's consumption has decreased by more than 25% in the last five years as the selection of scraps has improved to avoid mixtures between gold and platinum/palladium.

Production of Basic Metals

A use that was not identified in literature was suggested by **Company 27**. The company uses hydrazine hydrate as reducing agent for removing traces of selenium from process liquids. The process liquid is acidic filter press filtrate. The solution that is subject to filtration comes from precipitation of selenium with sulphur dioxide and, following hydrazine treatment, the filtrate is sent to a copper refinery electrolyte circuit. Copper refinery electrolyte cannot contain any dissolved selenium, as dissolved selenium would precipitate during electrolysis to copper cathodes. The selenium limit for LME grade A copper cathodes is 2 ppm and customers may even specify lower limits for selenium. With the use of hydrazine, the refinery is able to circulate filtrate directly without further purification treatment.

The concentration of hydrazine hydrate in the solutions used is 55% and its consumption of hydrazine hydrate solution in 2009 was in the 1-10 tonne range. There has been no discernible change to the company's consumption in the last five years. The concentration of the solution used is reasonably high to ensure that the volume stored on-site is kept low and is easier to handle.

4.4.2 Locations and Quantities Used

The number of companies involved in the use of hydrazine hydrate as a reductant for metals is unknown but is expected to be small, probably towards the lower end of the 10-100 range (based on consumption data for a number of key players in the EU market). Some of them, however, may consume considerable amounts of the substance in the production of precious metals and catalysts based on precious metals.

4.4.3 Structure of Supply Chain

Some information available for large players in this sector is summarised in Confidential Annex 2.

4.5 Use in Effluent Treatment

4.5.1 Description of Use

4.5.1.1 Information from Literature

As powerful reductive agents, hydrazine hydrate and its salts can be used as agents for effluent treatment, for example for the removal of contaminants such as Cl_2 , Br_2 , NO_x , and heavy metals from gaseous and aqueous streams (Arkema, 2005). Hydrazine has also been proposed as a reductant for the non-catalytic reduction of NO (Cho & Chang, 1997; Hamon, 2010).

4.5.1.2 Consultation Findings

No consultee has specifically confirmed the use of hydrazine hydrate in applications such as those described above. However, the reduction of metals (see Section 4.4.1 above) could be considered, under certain circumstances, as 'effluent treatment'. Such use of hydrazine hydrate has been confirmed and is discussed later in this Section.

4.5.2 Locations and Quantities Used

As regards effluent treatment, relevant users may include key water treatment companies; and key industrial customers (chemical plants, paper-mills, etc.) (Arkema, 2005). No much specific information has been obtained through consultation. As noted above, the Confederation of European Paper Industries (2010) suggests that hydrazine is not used in wastewater treatment in paper mills.

No information on quantities used is available. It is possible that other applications such as the use of hydrazine as a corrosion inhibitor and a reductant for metals may incorporate any tonnage consumed for effluent treatment purposes.

4.5.3 Recent and Future Trends

No information is available, which the exception of the input made by the Confederation of European Paper Industries and its members, as discussed above.

4.5.4 Structure of Supply Chain

No information is available.

4.6 Use in Paint, Ink and Dye Manufacture

4.6.1 Use in Paint and Ink Manufacture

It has been indicated that hydrazine hydrate may be used in the synthesis of paints and inks. Some additional – but limited – information is provided in Confidential Annex 2.

4.6.2 Use of Hydrazine/Phenylhydrazine as a Building Block of Organic Dyes

The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (2010) indicates that hydrazine, as well as phenylhydrazine, are used as precursors of N-heterocycles, which in turn can be used as building blocks in the synthesis of a small number of organic dyes.

When a dye manufacturer carries on the synthetic steps directly involving hydrazine / phenylhydrazine, these processes are typically conducted under strictly controlled conditions in closed systems, so that workers and environmental exposure are prevented¹⁵. These dyes can be used for paper and textiles (e.g. polyacrylic fibres colouration) (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers, 2010b). Production of such dyes could be taking place in Germany; however, the Association notes that, for many dyes, the actual production site is outside the EU. Notably, the Association does not represent all EU dye manufacturers either (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers, 2010b).

No significant contamination of the final dye with hydrazine or phenylhydrazine is to be expected. All the hydrazine/phenylhydrazine is converted and, in any case, in the isolated dye intermediate of a multi-step synthesis, contents below the detection limit of < 10 ppm are the norm (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers, 2010b).

4.7 Use in Purification Applications

Company 33 has confirmed that hydrazine hydrate can be added to sulphuric acid for purification purposes. Some additional – but limited – information is provided in Confidential Annex 2.

¹⁵ It is recognised that this use could arguably fall under the "synthesis" group of hydrazine hydrate applications.

4.8 Use in Aerospace Applications

4.8.1 Description of Use

4.8.1.1 Information from Literature

Hydrazine propellants were first developed by Germany for powering prototype jet engines in the Messerschmitt ME163 (during World War II) (Matunas, 2004). During the 1940s and 1950s, efforts focused on evaluations of monopropellants such as hydrogen peroxide, propyl nitrate, ethylene oxide and hydrazine. The US Jet Propulsion Laboratory (JPL) championed the use of hydrazine in the Voyager spacecraft in the 1970s and hydrazine eventually became the monopropellant of choice for small engines of spacecraft in attitude, on-orbit manoeuvring and gas generator applications (Hawkins *et al*, 2010). Hydrazine can, in theory, be used in both monopropellants and bipropellants.

Hydrazine Monopropellants

Hydrazine is an excellent storable fuel but also an excellent monopropellant when decomposed by a suitable solid catalyst. This catalyst often needs to be preheated for fast start-up or for extending the useful catalyst life. Iridium or porous alumina base are reportedly effective catalysts at room temperature. At elevated temperature, many materials decompose hydrazine, including iron, nickel and cobalt. The catalytic decomposition of hydrazine can be simplistically described as follows:

 $3 \text{ N}_2\text{H}_4 \rightarrow 4(1-x) \text{ NH}_3 + (1+2x) \text{ N}_2 + 6x \text{ H}_2$

where x is the degree of ammonia dissociation which is a function of the catalyst type, size and geometry, the chamber pressure, and the dwell time within the catalyst bed. The best specific impulse is attained when little ammonia is allowed to dissociate (Sutton & Biblarz, 2010).

Hydrazine monopropellant thrusters are used when system simplicity is important and moderate performance is acceptable (Sutton & Biblarz, 2010). Hydrazine monopropellant is used in satellite propulsion and the upper stages of satellite launchers. Literally hundreds of satellites and space probes rely on hydrazine fuelled thrusters for altitude control or orbit maintenance. Such precise manoeuvres require as little as a tenth of a pound of thrust, hundreds of times, over an operating lifetime of 10 to 15 years (Arch, 2010e). Monopropellant systems are also used on short-term missions. They provide altitude and roll control of boosters and upper states of expendable launch vehicles (Arch, 2010e).

Thrusters for satellites, spacecraft, space probes and launch vehicle attitude control that are based on hydrazine are available in 0.5 N to 400 N versions. The 'work horse' thrusters selected for the majority of programmes are the 1.0 N, 20 N and 400 N thrusters (Astrium, 2010).

Box 4.2: Examples of Current Uses of Hydrazine Propellants in the EU

Galileo

Galileo will be Europe's own global navigation satellite system, providing a highly accurate, guaranteed global positioning service under civilian control. It will be inter-operable with GPS and GLONASS, the two other global satellite navigation systems. The fully deployed Galileo system consists of 30 satellites (27 operational + 3 active spares). As a further feature, Galileo will provide a global Search and Rescue (SAR) function, based on the operational COSPAS-SARSAT system.

Two experimental Galileo satellites – GIOVE-A, GIOVE-B and GIOVE-A2 – are part of the first step in the in-orbit validation of the Galileo system. GIOVE-A was orbited by a Soyuz launcher from the Baikonur cosmodrome on 28 December 2005. The GIOVE-B satellite is using a hydrazine propulsion system with one tank containing 28 kg.

ADM-Aeolus

Hydrazine Bipropellants

In bipropellant systems, liquid hydrazine and an oxidiser are injected simultaneously to initiate a hypergolic reaction. Such systems can help power expendable launch vehicles such as Titans, Delta and Ariane 4, as well as the Space Shuttle orbital manoeuvring system and many large satellites (Arch, 2010e).

Aerozine-50 is a 50:50 mixture of UDMH and anhydrous hydrazine. It has been used in the second stage of the Delta II and Titan II, III, IV, and V family of launch vehicles (Zelnick *et al*, 2003; Meyer *et al*, 2007). UDMH may also be mixed with 25% hydrazine hydrate.

4.8.1.2 Consultation Findings

The use of anhydrous hydrazine in monopropellants (and to an extent in bipropellants, although it is clear that the use of the substance as a monopropellant is far more important (Swedish Defence Research Agency, 2010)) has been confirmed by consultees. The European Space Agency, and more specifically the Agency's Materials & Processes Working Group, coordinated the input of several leading companies within the EU aerospace industry sector that handle and use hydrazine as a propellant. The majority of this information is commercially sensitive and is thus presented in Confidential Annex 2.

4.8.2 Locations and Quantities Used

Some useful information from Caramelli (2008) on the identities of suppliers of hydrazines is provided in Confidential Annex 2. Information of a non-confidential natures includes the

testimony of **Company 25** which imports a small amount of anhydrous hydrazine ($<0.1 \text{ t/y}^{16}$) from a Chinese manufacturer for own use.

Discussions with industry consultees and the European Space Agency would indicate an overall EU consumption of anhydrous hydrazine below 10 t/y.

4.8.3 Recent and Future Trends

For companies that work on alternative monopropellants, such as **Company 25**, consumption of hydrazine has been on the decline. However, this may not be universally true, as discussed in Confidential Annex 2, where a considerable amount of detail is provided.

4.8.4 Structure of Supply Chain

Available information is provided in Confidential Annex 2.

4.9 Use in Defence Applications

4.9.1 Description of Use

4.9.1.1 Information from Literature

Fighter Jet Emergency Power Units

A blend of 70% hydrazine and 30% water, known as H-70 fuel, is used to operate the F-16 emergency power unit (EPU), where hydrazine allows the aircraft to maintain electrical and hydraulic power during periods of engine shutdown. The H-70 tank carries 56 pounds (25 kg) of fuel (i.e. 17.5 kg of hydrazine) and requires servicing after the fuel has been used (Zelnick *et al*, 2003).

As described in US literature, H-70 tanks are removed from the aircraft when the fuel is depleted below a level specified by the using activity. The tanks are delivered to the servicing facility where any remaining fuel is drained into a closed 55-gallon (210 L) stainless steel drum. The aircraft H-70 tank is filled using a closed system charging unit and is either returned to the aircraft or placed in a handling/storage container for future use. The bulk H-70 storage tank is a 55-gallon (210 L) stainless steel drum containing approximately 51 gallons (190 L) of H-70. Nitrogen gas is used as an inert pressure head in the bulk drum to transfer H-70 to the charging unit. An F-16 tactical wing is expected to use approximately 100 gallons (380 L) of H-70 per 20,000 flight hours with an additional minimum of 150 gallons (570 L) held in reserve to handle deployment/safety stock requirements (US Department of Defense, 1999). This information is based on a publication by the US military; it is expected that EU national air forces would have in place similar procedures as the aircraft are essentially the same across the world (at least as far as the EPU appears to be concerned).

¹⁶ Data have been provided for two years, 2003 and 2010.

Submarine Rescue System Gas Generators

Hydrazine is used in the RESUS (REscue system for SUbmarineS) submarine rescue system. RESUS is an independent, on-board submarine rescue system enabling buoyancy from any depth under emergency situations. RESUS enables the rapid buoyancy and rescue of an entire submarine and from any depth. RESUS is designed to blow the main ballast tanks of the submarine within a very short time – typically within 13-20 seconds (Astrium, 2010c).

Hydrazine is used in the gas generators of the liquid propellant type. The gas generators are located in the fwd and aft¹⁷ main ballast tanks (Astrium, 2010b). The working principle of the liquid propellant gas generators is based on the catalytic decomposition of hydrazine into a hot gas pressurant (Astrium, 2010c). The composition of the gas generator is shown in **Table 4.7**.

Characteristic	Liquid propellant
Propellant	Hydrazine
Propellant mass	62 kg
Outlet temperature	775 K
Gas composition	H_2 (46%); N_2 (28%); NH_3 (20%); H_2O (6%)
Quantity required*	Ca. 10

When the system is activated, the gas generators produce a hot gas that is cooled and directed by ducts to the top of the main ballast tanks. The very high pressure gas entering the main ballast tanks, rapidly evacuates the ballast water causing the submarine to become quickly buoyant. Subsequently, the submarine is stabilised, its attitude restored and the boat safely rises to the surface. The gas generators in the aft main ballast tanks stabilise the boat when surfaced (Astrium, 2010c).

4.9.1.2 Consultation Findings

The use of hydrazine in fighter jets has not been confirmed by consultees, but it is a widely known fact (often discussed in several Internet forums focused on military matters).

The combined input received from the European Space Agency confirms that hydrazine is indeed used in submarine rescue systems currently operated by a small number of navies in the EU. Some additional information is provided in Confidential Annex 2.

¹⁷ Fwd is towards the front while aft is towards the stern (rear) of the vessel.

4.9.2 Locations and Quantities Used

4.9.2.1 Fighter Jet Emergency Power Units

A total of 3,072 F-16 aircraft are active around the world¹⁸. A total of 4,428 F-16s had been produced by early 2010, the vast majority of which on the Fort Worth production line in the USA: 3,501 airframes, or roughly 79% of the total (F-16 Net, 2010).

When volume production started for the first customers (USAF and the European Participating Air Forces), two European production lines were involved as well, as part of a compensation package. Both SABCA in Belgium and Fokker in the Netherlands produced parts (both for European and USAF airframes), and were responsible for the assembly of the European F-16s: SABCA for Belgian and Danish F-16s, Fokker for Dutch and Norwegian F-16s. SABCA produced a total of 222 airframes (covering roughly 5%) and Fokker produced 300 airframes (covering 7%).

In early 2010, only the Fort Worth line remained open. F-16 Net (2010) suggests no production has taken place in the EU since 1992.

Table 4.8 shows the number of F-16 fighter jets operated by EU Member States (plus Norway). Eight countries have such aircraft in their fleets with the largest numbers belonging to the Hellenic Air Force and the Royal Netherlands Air Force.

Country	Number of active F-16 aircraft	Country	Number of active F-16 aircraft
Belgium	72	Norway	56
Denmark	62	Portugal	45
Greece	170	Poland	48
Italy	34 (on lease)	Total	595
Netherlands*	108		
Source: F-16	Net, <u>http://www.f-16.net/f-16_users.h</u>	<u>atml</u>	

As discussed earlier, the F-16 H-70 tank carries 17.5 kg of hydrazine; therefore, the total of 595 aircraft shown in the table must carry $595 \times 0.0175 = 10.4$ tonnes of hydrazine at any one time. Some additional quantity must be stored in military air bases to replenish the tanks, after the propellant is used. No information is available on what the relevant quantity might be neither is it possible to estimate the rate of replenishment.

¹⁸ See here: <u>http://www.f-16.net</u>

4.9.2.2 Submarine Rescue System Gas Generators

The hydrazine gas generators that we have identified are manufactured in Germany. It is suggested that, for over 25 years, RESUS has been standard equipment installed in all German submarines. RESUS has also been installed on the submarines classes 206A, 209-1200, 209-1400, 209-1500, 212A and 214. RESUS can also be retrofitted to Russian submarines 877EKM (Kilo Class) and installed into the new Amur-Class, irrespective of the very different geometry of ballast tanks (Astrium, 2010c).

Apart from Germany, other countries the submarines of which may be fitted with hydrazinebased RESUS include Greece, Italy, India, Israel, South Korea and Turkey (Astrium, 2010d). **Table 4.9** shows the numbers of relevant submarines in EU national fleets.

Table 4.9: Classes	of Submarines that may	contain Hydrazine Gas Gen	erators (RESUS)				
Country		Submarine class					
	209A-1200	212A	214				
Germany		4 in service – 2 planned					
Greece	4 in service		1 completed – 3 planned				
Italy		2 in service – 2 planned					
Source: Wikipedia a	rticles						
Note: six submaring http://www.defensen	es of the 206A type opera <u>ews.com/story.php?i=465</u>	ted by the German Navy are t 16689	o be decommissioned, see:				

Assuming that each submarine requires on average 10 gas generators and that the entire propellant (62 kg per generator) is made of anhydrous hydrazine¹⁹, the assumed total of 11 submarines in service or completed would contain up to $11 \times 10 \times 0.062 = 6.8$ tonnes. The amount of hydrazine consumed each year in the manufacture of submarine rescue system gas generators is assumed to be included in the consumption of hydrazine in the aerospace sector. In any case, the number of relevant vessels is rather small and it has not been confirmed whether all or only some of the identified vessels contain hydrazine gas generators.

4.9.3 Structure of Supply Chain

Although manufacture of the F-16 fighter jets currently takes place in the USA (and other non-EU countries), it is clear that the Air Forces of a small number of EU Member States need to have accessed to hydrazine mixtures for the replenishment of the EPU tanks. Information on the structure of this supply chain is not available.

The anhydrous hydrazine used in the manufacture of submarine rescue systems is largely the same material used in aerospace applications (see more detail on this in Confidential Annex 2). Therefore, the supply chain upstream from the manufacturer of the RESUS system must be

¹⁹ This is further clarified in Confidential Annex 2.

essentially the same. Downstream, it is expected that the RESUS system is supplied to the submarine manufacturer²⁰.

4.10 Other Uses

4.10.1 Use in Syntheses of Unclear Relevance to the EU

4.10.1.1 Photography Chemicals

Information from Literature

Silver halide photographic systems which employ hydrazines have been proposed in patent literature. These hydrazine-containing systems may be based on phenylformylhydrazine and derivatives thereof. These hydrazine-containing systems can produce the desired ultra-high contrast effects and are considerably faster than conventional litho systems (Fodor, 1992). Hydrazine itself has been mentioned by Jones (1974) as a very faint developer in an alkaline solution and it is mentioned that neither itself nor its organic derivatives are practically used. Jones acknowledges however that some of its compounds had been suggested as an addition to haloid emulsions without free silver, in order to obtain intense vigorous images. DMcT, mentioned above in relation to lubricants, has also been discussed as a general photographic chemical. Old literature sources suggest that DMcT and its disodium salt (II) were used to form silver salts that stabilised photographic layers. Several patents have reportedly been filed in relation to the use of DMcT (NTP, 2005)

Consultation Findings

Communication with Imaging and Printing Europe (2010), the relevant trade association, confirms that in old literature one can find hydrazine (but more often hydrazine dihydrochloride, $N_2H_4.2HCl - EC$ Number: 226-283-2, CAS Number: 5341-61-7) as a substance used in photographic developers, mainly in graphic/reprographic applications²¹. However, such uses are most likely to be historical only. A check performed by the association on the European inventories of a large photographic chemicals company (a film- paper-, plate- and complete photochemical- production chemicals database) showed no result for hydrazine or hydrazine dihydrochloride. Similarly, neither hydrazine nor hydrazine dihydrochloride are listed in the association's "Code of Practice", which is a common shared inventory of the European photographic industry. Two large companies in the photography industry (**Company 3** and **Company 4**) have also confirmed that hydrazine is not used in their products.

²⁰ The manufacturer of the submarine types identified in **Table 4.9** is Howaldtswerke-Deutsche Werft (HDW), a German shipbuilding company, headquartered in Kiel.

²¹ A publication authored by Baumann, an academic from the University of Dortmund was referred to as mentioning the use of hydrazine in lithographic processes. However, the said publication was published for the last time in 1991.

4.10.1.2 Anti-oxidants

Several anti-oxidant and metal deactivator compounds contain the hydrazine moiety. Its property as a base and as a reducing agent aid in this function (Arch, 2010j). These uses have not been confirmed as relevant to the EU.

4.10.1.3 Flame Retardants

Several patents of flame and scorch retardant formulations that contain DMcT have been filed including such for (a) fire retardant compositions for wildfire suppression that are based on salts of thiosulphuric acid and contain DMcT (presumably as a stabiliser or the corrosion inhibitor), (b) coloured liquid fire retardant compositions for aerial application to vegetation, (c) concentrates for fire-resistant hydraulic fluids containing DMcT in low concentrations where it acts as a corrosion inhibitor (e.g., for aluminium), (d) flame retardants for nylon 66 where DMcT salts of barium, cobalt, nickel, manganese, copper, chromium, iron, and zinc gave good fireproofing, and (e) smoke suppressant additives for polyurethane foam where the final foam contained about 6% DMcT derivative. DMcT monobenzoate provided anti-scorching protection to halogen-containing polymers (NTP, 2005). Specific information for the EU has not been identified.

4.10.1.4 Oil Stimulation Agents

It has been suggested that salts of hydrazine may be used as oil-well treatment-stimulation agents (Arkema, 2006). Haws *et al* (1975), in a rather old patent, also refer to their use in a process for increasing the injectivity index in oil wells. In a somewhat different context, Fink (2003) refers to hydrazine as an oxygen scavenger suitable for use in drilling operations, well workover, and cementing. These uses have not been confirmed as relevant to the EU.

4.10.2 Use in Shipping

Company 11 has indicated that hydrazine is used in closed warm water systems in ships. No further detail is available, although it is reasonable to believe that the substance may be used as a corrosion inhibitor.

4.10.3 Use in the Recovery of Gold from Ores

4.10.3.1 Information from Literature

It is suggested that the substance (solutions of hydrazine hydrate with a concentration of 55% or 60%) is used in the Actired® process for gold and silver recovery from ores. Actired® is used to improve processes (Zadra or Anglo-American) for gold and silver recovery from ores by activated carbon elution (Arkema, undated and Harvey *et al*, 1998). Industrial use of the process in France, at 95°C showed that there was a ten-fold decrease in the cyanide consumption, an energy and reagent gain, elution efficiencies systematically greater than 98% and a 50%

reduction in elution time (Duparque, 1995). Nevertheless, the mine that used this process closed in 1995²².

4.10.3.2 Consultation Findings

The company that has been behind the development of the Actired® process, **Company 7**, was contacted for the purposes of this study. The company has claimed that the patent for the process which was filed by the company itself in 1995, has never been industrially applied – the company was never approached by any other company with a request to grant a licence, therefore the probability that it is applied anywhere in the world is low, and if so, it is beyond **Company 7**'s knowledge. Notably, since a few years, the company does not maintain the patent (i.e. it does not pay the annual duties to preserve its intellectual property rights) thus the process in now in the public domain. Overall, it appears rather unlikely that hydrazine currently finds use in this application.

4.10.4 Use in the Semiconductor Industry

4.10.4.1 Information from Literature

Chemical Bath Deposition for Thin Film Formation

The use of hydrazine in the deposition of thin films is reported in several sources, for example:

- Sasani Ghamsari *et al* (2006) discuss polycrystalline nanostructured PbS thin films deposited on a glass substrate when hydrazine hydrate is used as a reducing agent;
- Ben Nasr *et al* (2006) and Gangopadhyay *et al* (2007) discuss hydrazine as complexing agent for the chemical bath deposition of ZnS, including for monocrystalline silicon solar cells; and
- Hankarea *et al* (2009) mention the use of hydrazine hydrate for the chemical bath deposition of polycrystalline WSe_2 semiconductor thin films.

Hydrazine derivatives, such as phenylhydrazine and dimethyl hydrazine may also be used in vapour deposition techniques (Seshan, 2001).

Hydrazine as a Solvent for Semiconductor Material (Photovoltaics)

Scientists at IBM reportedly developed a technique for spin-coating substrates with a layer of metal chalcogenide²³ semiconducting film just 5 nm thick. IBM discovered a way of dissolving metal chalcogenide films – which have higher mobility – in hydrazine (Kalaugher, 2004).

This work appears to be progressing with more papers being published. As reported by Edwards (2010), IBM has now developed a prototype solar cell that uses common, inexpensive elements and an inexpensive manufacturing process that involves hydrazine solutions. The new

²² See here: http://www.ademe.fr/difpolmine/Difpolmine_RapportFinal/communication/14_posters/Difpolmine_Poster01_Historic.p

<u>df</u>

 $^{^{23}}$ Chalcogen refers to four chemical elements in one column of the periodic table – oxygen, sulphur, selenium and tellurium. Some metal chalcogenides (such as cadmium sulphide, tin selenide and zinc telluride) are well-known high-performance semiconductors (IBM, 2004).

photovoltaic cells are known as "kesterite" cells; these are produced using a printing technology in which a solution containing nanoparticles is spin-coated onto a glass substrate. According to IBM, their efficiency is close to that of established solar cells. While the current technology uses the rare elements indium and tellurium (the former in short supply), these cells uses the common elements tin, zinc, copper, selenium, and sulphur.

Hydrazine as an Anisotropic Etchant of Silicon

Bulk micromachining of silicon uses wet- and dry-etching techniques in conjunction with etch masks and etch stops to sculpt micromechanical devices from the Si substrate. One of the key capabilities that make bulk micromachining a viable technology are anisotropic etchants of silicon, such as ethylene-diamine and pyrocatechol (EDP), potassium hydroxide (KOH), and hydrazine (Vittorio, 2001).

Hydrazine as as Dopant for Semiconductors

Hydrazine has also been referred to as a n-dopant for semiconductors. Derivatives such as dimethylhydrazine may also be used for this purpose (Fthenakis & Bowerman, undated; Wang RY *et al*, 2008). Kropewnicki & Kohl (1998), Berkovits *et al* (2002) and others discuss the use of hydrazine-based solutions for the nitridation of GaAs substrates.

4.10.4.2 Consultation Findings

The European Semiconductor Industry Association (2010) has suggested that it currently has no information confirming that hydrazine is being used by EU semiconductor manufacturers.

4.10.5 Use in Vehicle Fuel Cells

4.10.5.1 Information from Literature

Engineers at the Daihatsu unit of Toyota, located in Ryuo, Japan, were reported as developing a fuel cell that uses hydrazine hydrate, rather than hydrogen, to power automobiles and other motorised vehicles (Atkins, 2007). In addition, Italy-based catalyst manufacturer Acta demonstrated a few years ago that a fuel cell using hydrazine can deliver a peak power of 700 mW/cm², using platinum-free HYPERMEC catalysts²⁴. This exceeded by 40% the 500 mW/cm² reported for Daihatsu power cells under the same operating conditions. According to Acta, this was sufficient improvement to allow hydrazine-fuelled cells to replace hydrogenfuelled cells in existing cars and buses (Nguyen, 2008).

4.10.5.2 Consultation Findings

Communication was established with Fuel Cell Europe, the European association representing the fuel cell sector. The association enquired among its members and has advised that according to those consulted (including the Joint Research Centre of the European Commission

²⁴ HYPERMEC is a platinum-free catalyst which works with hydrogen and methanol but also has the ability to work with ethanol and ethylene glycol (as shown here: <u>http://www.fuelcelltoday.com/online/industry-directory/organisations/ac/Acta</u>).

(Institute for Energy)), hydrazine is not considered or developed at the moment by European fuel cells industry actors. Projects in the past may have occurred but never passed the R&D stage. This is mainly due to the very instability of the fuel and its highly flammable nature. It is of note that the European Research, Technological Development and Demonstration Activities (RTD&D) Programme of Europe (Fuel Cells & Hydrogen Joint Undertaking²⁵) for 2008-2013 has not identified hydrazine as a topic of research (Fuel Cell Europe, 2010).

4.10.6 Use in Soldering Fluxes

4.10.6.1 Information from Literature

Several sources, for instance Goh & Ng (1987), suggest that hydrazine may be a component of soldering fluxes. It is likely that hydrazine salts rather than hydrazine hydrate itself may have found use in such fluxes. ILO (undated) suggests that hydrazine sulphate is an antioxidant in soldering flux for light metals and Welding Technology Machines (undated) suggest that bromide salts are very active and promote excellent wetting. WTIA (undated) refers to the use of hydrazine hydrobromide as well.

4.10.6.2 Consultation Findings

Despite efforts to communicate with selected suppliers of soldering materials, no specific information on the use of hydrazine or of its derivatives was obtained.

4.10.7 Use in Explosives and Ammunition Propellants

4.10.7.1 Information from Literature

Astrolite

When stoichiometrically mixed with ammonium nitrate, <u>anhydrous hydrazine</u> forms a powerful liquid explosive known as Astrolite. Astrolite G and Astrolite A/A-1-5 (with 20% aluminium additive - aluminium powder, 100 mesh or finer) are called also "liquid land mine" or "binary explosive". The explosive strength of such mixtures is very high; the detonation velocity of Astrolite G is 8,600 m/s and of Astrolite A/A-1-5 is 7,800 m/s (Meyer *et al*, 2007).

The explosive was apparently developed for the purposes of mining and drilling. Astrolite was considered 'safe' because its two components could be stored and transported separately, to be mixed only immediately before use. However, it was never widely adopted as a high explosive (Lewis, 2010) but may have been used in landmines. For instance, the Mine Action Information Center (2010) indicates that Astrolite G was used in a remotely-controlled, concealed (buried), pop-up, high-explosive, fragmenting, antipersonnel landmine (A/E 25P-1 (MLU-54E); and Training Unit, A/E 25P-1 (T-1)) by the US military. This is a 9.1 kg mine with an explosive load of 510 g.

²⁵ See here: <u>http://ec.europa.eu/research/fch/pdf/fch_ju_multi_annual_implement_plan.pdf</u>.

Hydan

Hydan is a smokeless binary liquid explosive of <u>hydrazine hydrate</u> and ammonium nitrate. It was reportedly developed by Dynamit Nobel Wien in 1994. For a mixture of 50:50, the detonation velocity obtained is 7,150 m/s (Meyer *et al*, 2007).

Despite a favourable price, high security and stability when stored separately, these explosive mixtures found no civilian market due to the handling problems of hydrazine hydrate. Japanese and US institutions have worked on similar mixtures for the use as propellants in ship artillery (Meyer *et al*, 2007). Communication with **Company 53** confirms that Hydan seems to have attracted interest only in military uses.

Explosive Derivatives

Hydrazine nitrate has a detonation velocity of 8,690 m/s. Mixtures with Octogen²⁶ pressed to high density reportedly reach velocities of >9,000 m/s (Meyer *et al*, 2007).

Meyer *et al* (2007) also refer to the use of hydrazine in the manufacture of aminoguanidine explosives such as:

- nitroaminoguanidine (CH₅N₅O₂), with a specific energy of 114.5 mt/kg = 1,124 kJ/kg, is obtained by reacting nitroguanidine with hydrazine in aqueous solution. Nitroaminoguanidine has gained a certain attractiveness as a reduced carbon monoxide propellant because of its ready ignitability and its burn-up properties; and
- triaminoguanidine nitrate (CH₉N₇O₃) is prepared by reacting one mole of guanidine dinitrate with 3 moles of hydrazine hydrate at 100°C for four hours. The product is distinguished by high contents of hydrogen and nitrogen and serves as an ingredient for low vulnerability ammunition (LOVA) gun propellants with high force but comparable low combustion temperature.

4.10.7.2 Consultation Findings

No company among the several contacted did confirm the use of hydrazine in explosives in the EU. Members of the Federation of European Explosives Manufacturers (2010) advised that hydrazine is not of relevance to the production of commercial explosives in the EU.

4.10.8 Use in Automotive Air Bag Gas-forming Agents

4.10.8.1 Information from Literature

There are several references on the Internet suggestion that sodium azide, the gas-forming agent in air bags, is produced from hydrazine by reaction with sodium nitrite (Schirmann & Bourdauducq, 2002).

²⁶ Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, also known as cyclotetramethylene-tetranitramine, tetrahexamine tetranitramine, or HMX.

4.10.8.2 Consultation Findings

Consultation with three key manufacturers of automotive air bags (**Companies 39, 40** and **41**) did not confirm the use of hydrazine in such application. A similar (negative) response was received from the European Automobile Manufacturers Association (2010).

4.11 Other Information – Member State Authorities

Some information on the manufacture, import and use of hydrazine and its mixtures has been provided by the Swedish Chemicals Agency (2010). This is summarised in **Table 4.10**.

Product	Manufacture	Imports		Consumption	Applications	
Tiouder	(tonnes)	(tonnes) Tonnes Origin (tonnes)		rippiloutions		
Mixtures (0.002- 64% hydrazine by weight)	70	43	EU	99	Corrosion inhibitors, paints incl. raw material,	
contained hydrazine is	0.33	13.7		13.8	other types of products	

4.12 Summary of Use

Table 4.11 provides an overview of manufacture, uses and recycling of the substance as well as the NACE codes and REACH use descriptions for the relevant activities.

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU						
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product
Manufacture of hydrazine hydrate	NACE: C20.1 – Manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms	Manufacture	N/A	N/A	N/A	64% max
Uses definitely or reason	nably confirmed as relevant to the EU					
Synthesis of hydrazine derivatives (also see some individual derivative uses below)	 NACE: C20.1 – Manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms Sector of Use: SU8 – Manufacture of bulk, large scale chemicals Chemical Product Category: PC19 – Intermediate 	Formulation	Yes	Intermediate use	Hydrate	Nil (?) in end product
Synthesis of pharmaceuticals	 NACE: C21.1 - Manufacture of basic pharmaceutical products Sector of Use: SU9 – Manufacture of fine chemicals Chemical Product Category: PC29 – Pharmaceuticals 	Formulation	Yes	Intermediate use	Hydrate	Nil in end product
Synthesis of agrochemicals	 NACE: C20.2 - Manufacture of pesticides and other agrochemical products Sector of Use: SU9 – Manufacture of fine chemicals Chemical Product Category: PC27 – Plant protection products 	Formulation	Yes	Intermediate use	Hydrate	Nil in end product

Table 4.11: Overview	Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU							
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product		
Synthesis of chemical blowing agents	 NACE: C20.1 – Manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms Sector of Use: SU8 – Manufacture of bulk, large scale chemicals Chemical Product Category: PC32 – Polymer preparations and compounds 	Formulation	Yes	Intermediate use	Hydrate	Nil in end product		
Monomer in PUR/acrylics synthesis	 NACE: C20.3 – Manufacture of paints, varnishes and similar coatings, printing ink and mastics C20.5.2 – Manufacture of glues Sector of Use: SU10 – Formulation [mixing] of preparations and/or re-packaging (excluding alloys) Chemical Product Category: PC1 – Adhesives, sealants PC9a – Coatings and paints, thinners, paint removers 	Formulation	Yes	Intermediate use	Hydrate	Very low**		
Monomer in polymer synthesis for lubricant formulations	 NACE: C20.5.9 - Manufacture of other chemical products n.e.c. Sector of Use: SU10 – Formulation [mixing] of preparations and/or re-packaging (excluding alloys) Chemical Product Category: PC24 – Lubricants, greases, release products 	Formulation	Yes (in the production of the polymer)	Intermediate use	Hydrate (?)	Assumed to be low (if any)		

Table 4.11: Overview	able 4.11: Overview of Manufacture / Uses of Hydrazine in the EU					
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product
	NACE: C29.3.2 – Manufacture of other parts and accessories for motor vehicles (uncertain)					
	Sector of Use: SU3 – Professional uses (uncertain)	End use	No			
	Chemical Product Category : PC24 – Lubricants, greases, release products					
	NACE: C20.1 – Manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms					
Treatment of nuclear reactor waste	Sector of Use: SU8 - Manufacture of bulk, large scale chemicals (including petroleum products)	Formulation	Yes (hydrazine mononitrate)	Intermediate use	Derivatives (from hydrate)	Nil in end product
	Chemical Product Category : PC20 – Products such as pH-regulators, flocculants, precipitants, neutralization agents					

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU							
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product	
Corrosion inhibitor in water treatment	 NACE: C20.1 – Manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms Sector of Use: SU10 – Formulation [mixing] of preparations and/or re-packaging (excluding alloys) Chemical Product Category: PC37 – Water treatment chemicals 	Formulation	No (dilution and possible addition of catalyst)	Hydrazine partly used to be intentionally transformed	Hydrate	Hydrazine hydrate solutions 5-55% (3%-35%	
	 NACE: D35.1.1 - Production of electricity Sector of Use: SU23 – Electricity, steam, gas water supply and sewage treatment Chemical Product Category: PC37 – Water treatment chemicals 	End use	Yes (N ₂ , H ₂ O, NH ₃)	(decomposed) to ammonia for pH regulation		hydrazine)	

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU							
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product	
Reducing agent in surface metallisation (metal deposition, electrolytic & electroless)	 NACE: C25.6 – Treatment and coating of metals; machining C22.2 – Manufacture of plastics products C23.1.9 – Manufacture and processing of other glass, including technical glassware Sector of Use: SU12 – Manufacture of plastics products, including compounding and conversion; SU13 – Manufacture of other non-metallic mineral products, e.g. plasters, cement; SU15 – Manufacture of fabricated metal products, except machinery and equipment Chemical Product Category: PC14 – Metal surface treatment products, including galvanic and electroplating products PC15 – Non-metal-surface treatment products 	Formulation	Yes (probably N ₂ & H ₂ O)		Hydrate	Nil in end product (low presence in bath)	
Reducing agent in precious metal recovery	 NACE: C24.4.1 – Precious metals production Sector of Use: SU14 – Manufacture of basic metals Chemical Product Category: PC7 – Base metals and alloys 	Formulation	Yes (N ₂ & inorganics)**		Hydrate	Very low to nil in end product**	
Reducing agent in basic metal recovery	 NACE: C24 – Manufacture of basic metals Sector of Use: SU14 – Manufacture of basic metals Chemical Product Category: PC7 – Base metals and alloys 	Formulation	Yes (N ₂ & inorganics)**		Hydrate	Nil in end product	

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU							
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product	
Reducing agent in purification of chemical reagents	 NACE: C20.1.3 – Manufacture of other inorganic basic chemicals Sector of Use: SU8 – Manufacture of bulk, large scale chemicals Chemical Product Category: PC0 – Other 	Formulation	Yes**		Hydrate	Low**	
Paint and ink manufacture**	 NACE: C20.1.3 – Manufacture of other inorganic basic chemicals Sector of Use: SU8 – Manufacture of bulk, large scale chemicals Chemical Product Category: PC0 – Other 	Formulation (mixing)	Partially (as stabiliser)	Paint/ink manufacture – intermediate use	Hydrate	Nil**	
	 NACE: C20.3 – Manufacture of paints, varnishes and similar coatings, printing ink and mastics Sector of Use: SU8 – Manufacture of bulk, large scale chemicals Chemical Product Category: PC9a – Coatings, and paints, thinners, paint removers PC18 – Ink and toners 	Formulation	Yes**				

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU							
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product	
Synthesis of organic dyes	 NACE: C20.1.2 – Manufacture of dyes and pigments Sector of Use: SU8 – Manufacture of bulk, large scale chemicals Chemical Product Category: PC34 – Textile dyes, finishing and impregnating products; including bleaches and other processing aids 	Formulation	Yes (phenyl- hydrazine and N- heterocycles)	Intermediate use	Derivatives (from hydrate)	Close to nil in end product (< 10 ppm)	
Laboratory chemical reagent	 NACE: M72 – Scientific research and development Sector of Use: SU24 – Scientific research and development Chemical Product Category: PC21 – Laboratory chemicals 	Formulation/ End use	Probably	R&D use	Hydrate	Unknown	
Propellant for aerospace vehicles	 NACE: C30.3.0 – Manufacture of air and spacecraft and related machinery Sector of Use: SU17 – General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment Chemical Product Category: PC13 – Fuels 	Formulation (end use, launching of satellites outside the EU)	No (into $N_2 \& H_2$ when in use outside the EU)	Defence issues	Anhydrous	ca. 100% (50% in Aerozine mixtures)	
Fighter jet Emergency Power Units	NACE: C30.4.0 - Manufacture of military fighting vehicles Sector of Use: SU17 – General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment Chemical Product Category: PC13 – Fuels	End use	Yes (N ₂ & H ₂)	Defence issues	Anhydrous	ca. 100%	
ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU						
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product
Submarine rescue system gas generators	 NACE: C30.4.0 - Manufacture of military fighting vehicles Sector of Use: SU17 – General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment Chemical Product Category: PC13 – Fuels 	Formulation	No	Defence issues	Anhydrous	High**
	NACE: No code Sector of Use: SU0 – Other Chemical Product Category: PC13 – Fuels	End use	Yes (H ₂ , N ₂ , NH ₃ , H ₂ O)			
Uses potentially relevan	t to the EU – Not discussed in detail in this report			·		
Use as component of warm water systems in shipping	 NACE: C30.1.1 – Building of ships and floating structures Sector of Use: SU17 – General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment Chemical Product Category: PC37 – Water treatment chemicals 	End use	?	Probably similar to the use as corrosion inhibitor	Hydrate (?)	Probably similar to the use as corrosion inhibitor
Reducing agent in effluent treatment	 NACE: E38.2.1 – Treatment and disposal of non-hazardous waste Sector of Use: SU3 – Industrial uses: Uses of substances as such or in preparations at industrial sites Chemical Product Category: PC20 – Products such as pH-regulators, flocculants, precipitants, neutralization agents 	End use	Yes (probably N ₂ & H ₂ O)	Probably similar to the use as corrosion inhibitor or metal reductant	Hydrate	Probably similar to the use as corrosion inhibitor or metal reductant

ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU							
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product	
Uses unlikely to be relevant to the EU – Not discussed further in this report							
Use as a solvent for metal dissolution for photovoltaics	 NACE: C27.9.0 – Manufacture of other electrical equipment Sector of Use: SU16 – Manufacture of computer, electronic and optical products, electrical equipment 	Formulation	No (?)		Hydrate	Unknown	
	Chemical Product Category: PC33 – Semiconductors						
Use as fuel in vehicle fuel cells	 NACE: C29.3.2 – Manufacture of other parts and accessories for motor vehicles Sector of Use: SU17 – General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment Chemical Product Category: PC13 – Fuels 	End use	Yes (N ₂ & H ₂)		Hydrate	ca. 100%	
Use as an antioxidant in soldering flux for light metals	 NACE: C25 – Manufacture of fabricated metal products, except machinery and equipment Sector of Use: SU15 – Manufacture of fabricated metal products, except machinery and equipment Chemical Product Category: PC38 – Welding and soldering products (with flux coatings or flux cores.), flux products 	Formulation	Yes (bromide salts)		Derivatives (from hydrate)	Unknown	

ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

Table 4.11: Overview of Manufacture / Uses of Hydrazine in the EU						
Manufacture / Use	NACE code / REACH use description	Stage of use	Trans- formation into another substance?	Issues pertaining to REACH authorisation*	Form of hydrazine	Presence of hydrazine in end product
Use as an explosive (in mixtures) for mining and ammunition (anti- personnel land mines)	 NACE: C20.5.1 – Manufacture of explosives C25.4.0 – Manufacture of weapons and ammunition Sector of Use: SU2a – Mining (without offshore industries) SU0 – Other (military) Chemical Product Category: PC11 – Explosives NACE: B7 - Mining of metal ores Sector of Use: SU2a – Mining (without offshore industries) SU0 – Other Chemical Product Category: PC11 – Explosives 	Formulation End use	Yes (hydrazine nitrate, amino- guanidines) Yes (N ₂ & H ₂)	Defence issues Intermediate use	Anhydrous Hydrate Derivatives (from hydrate)	Up to 50% in mixtures Probably nil in derivatives
Use as a precursor for air bag gas-forming substances * on the basis of claims	 NACE: C20.5.1 – Manufacture of explosives C29.3.2 – Manufacture of other parts and accessories for motor vehicles Sector of Use: SU17 – General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment Chemical Product Category: PC11 – Explosives made by industry stakeholders and current understanding of a 	Formulation	Yes (sodium azide) mentioned earlier	Intermediate use	Derivatives (from hydrate) t has not been po	Probably nil
this interpretation is in li (<u>http://guidance.echa.eu</u>	ine with the definition agreed by the Commission, the Member ropa.eu/docs/guidance_document/clarificationintermediates 2	States and ECH 201005_en.pdf)	HA on the 4 th May due to lack of det	2010 ailed information.	1	5

** additional detail is provided in Confidential Annex 2

5 RELEASES FROM USES OF HYDRAZINE

5.1 Releases to the Environment

5.1.1 Use in Water Treatment

5.1.1.1 Information from Literature

No literature information is available for EU-based installations. However, releases from nuclear power generating plants have been reported in Canada, where emissions from nuclear power plants appear to account for the majority of releases of hydrazine. Of all emissions from these plants (three plants), more than 90% was to water and the quantities disposed of were mainly sent off-site for incineration or physical or chemical treatment (Environment Canada & Health Canada, 2010). **Table 5.1** shows the concentrations of hydrazine in effluents from nuclear power plants in Ontario, Canada.

		Effluent concentration (mg/L)		Quantity of	Power	
Facility	Year	Yearly average	Yearly range	hydrazine released in effluent (kg/yr)	generated (in GWh)	
А	2006	0.01	0.003-0.03	570	19.100	
В	2006	0.005	0.003-0.02		17,100	
С	2006	0.004	0.02 (max)	271	26,970	
D	1995 - 2004	0.002	0.028 (max)	1,024	4,000	

This Canadian government publication explains how losses of hydrazine may occur. It is described that cooling water circuits of boilers of nuclear reactor facilities generate a liquid effluent containing hydrazine, which is released to the environment. Every day, there is partial removal of steam from the plant's condenser with replacement by fresh, demineralised water to maintain dissolved solids concentrations at constant low levels. This steam removal, called 'blowdown,' becomes part of the final effluent and contains hydrazine because this substance is used in stoichiometric excess to ensure removal of dissolved oxygen from the make-up water used to compensate the blowdown steam. The Canadian government notes that fossil-fuelled power generating stations in Canada use hydrazine in boiler feedwater systems as well (Environment Canada & Health Canada, 2010).

Use of hydrazine in feedwater treatment constitutes the major use of hydrazine in nuclear and fossil-fuelled power plants, but smaller quantities are also used by these facilities for corrosion and pH control in a variety of systems, including auxiliary boiler water, recirculating cooling water, emergency coolant injection and boiler lay-up. In principle, these other systems can also

generate and release liquid effluents to the receiving environment (Environment Canada & Health Canada, 2010).

The Canadian Government notes that potential environmental releases of hydrazine can occur from the auxiliary feedwater systems from other industrial plants making use of hydrazine in their boiler systems. In principle, these systems use much less hydrazine than that used to counter oxidation in cooling systems of boilers, i.e. power plants (Environment Canada & Health Canada, 2010).

5.1.1.2 Consultation Findings

A considerable amount of information is available from a company that operates power plants, **Company 26**. Due to its confidential nature, this is presented in Confidential Annex 3.

On the other hand, **Company 32** has advised that there are no known emissions of hydrazine to the environment from its nuclear power plants. Any excess hydrazine which does not react with oxygen disproportionates at high temperatures to yield inert plant tolerable substances, ammonia, water, nitrogen and hydrogen. Typically, steam outlet temperature from an AGR boiler is in the region of ca. 540°C and that for a PWR station is ca. 280°C.

The reagent is delivered in bulk containers, with a preference for pre-diluted reagent where this is appropriate. The company rigorously enforces the relevant national regulations to minimise personnel exposure to hydrazine. Handling/storage of this substance is further regulated by the regulations implementing the provisions of the Seveso II Directive and subsequently low volumes (maximum 1 tonne of a 55% solution) of hydrazine are stored at each power plant site at any one time²⁷.

Company 52, a power plant operator, estimates that no release to any environmental compartment occurs during the use of hydrazine hydrate solutions.

Company 19, a water treatment specialist company, suggests that hydrazine levels can normally not been measured in boiler blowdown water or steam in high-pressure boilers. It concedes, however, that, in theory, there may always be a level of non-decomposed hydrazine left. The company was not aware of the possible levels of hydrazine.

Company 44, a nuclear plant contractor, indicates that during the use of hydrazine hydrate in nuclear power plants for solids removal (consumption of the hydrate is at 0.1-10 t/y), less than 1 kg/y may be released to the atmosphere. Solutions that contain hydrazine hydrate are collected after use, are stored on-site in specific tankers before been treated in a dedicated centre. Hence, the company claims a nil release of hydrazine to the environment.

Finally, **Company 8**, a boiler maker, believes that when hydrazine is injected in the water cycle, the temperature increase inside the exchangers forces its decomposition into ammonia. Hence, in the company's view, releases should not be expected.

²⁷ We have been advised that, if a company holds 0.5 metric tonnes of hydrazine >5% on site, it becomes a Low Tier (Seveso) site and if 2 metric tonnes are held, it becomes a Top Tier site. Therefore, power stations that wanted to stay away from Seveso II Directive preferred a solution of less than 5% w/w of hydrazine. The only stations which take 55% w/w solutions are the nuclear sites which are Low Tier sites. They manage their inventories very carefully, as other chemicals are aggregated together in the Regulations that implement the Seveso II Directive. Essentially, the Regulations have forced some users towards more dilute hydrazine hydrate solutions, as generally powers stations do not want use the alternatives to hydrazine, due to poor performance.

5.1.1.3 Conclusion

The available information, from literature and consultation suggests that some releases to the environment might be expected during the use of hydrazine hydrate as a corrosion inhibitor. The relevant environmental compartments are the atmosphere and liquid effluent. Again, some additional information can be found in Confidential Annex 3.

5.1.2 Use as a Reducing Agent for Metals

5.1.2.1 Production of Precious Metals

Several companies have provided estimates on their releases of hydrazine hydrate during the precipitation of precious metals. The majority of this information is presented in Confidential Annex 3 and suggests very limited releases (if any) to the atmosphere and to liquid effluent. A further company, **Company 31**, which uses a very small amount of hydrazine in the recovery of precious metals, reported no emissions to any environmental compartment.

5.1.2.2 Production of Basic Metals

Company 27 uses hydrazine hydrate solutions for the removal of selenium from process effluents. It receives hydrazine hydrate solution and stores this in small plastic vessels (60-70 litres) in ambient temperature and dry conditions under roof in a dedicated room. The solution is fed into the process by pump directly from the storage vessel to the reactor tank. The vessel and pump are located in a separate, ventilated room.

The substance is consumed during the reaction process. The company estimates that releases of hydrazine to sewer and surface water are close to nil, as the process takes place within a closed system which does not give rise to water emissions.

5.1.3 Use in Aerospace Applications

Information has been provided by a number of companies involved in the processing of hydrazine propellants, the manufacture of thrusters and the refuelling of launchers. This is presented in Confidential Annex 3 to this report. In addition, **Company 25** has provided its estimates on the releases of hydrazine to the environment during its (limited) use in the manufacture of thrusters. The estimates (valid for the years 2003 and 2010) suggest a nil emission to all compartments (air, sewer, surface water, soil and waste). The company notes that hydrazine residues are destructed by combustion.

5.1.4 Use in Defence Applications

5.1.4.1 Fighter Jet Emergency Power Units

The Canadian Government notes that hydrazine fuel that is used in aircraft can be released into air and water as a result of accidental discharges on airfields. During international training exercises, allied countries flying F-16 aircraft may use and store small quantities of hydrazine

fuel at Canadian Forces bases. Allied forces are responsible for the management of the fuel and, in the event of an accidental discharge, for spill response (Environment Canada & Health Canada, 2010).

A US Department of Defense (1999) publication describes the engineering measures to be taken at military bases to prevent releases to the environment (architectural considerations, spill containment measures, piping and draining, and waste disposal methods).

No relevant information was collected through consultation.

5.1.4.2 Submarine Rescue System Gas Generators

No information is available.

5.1.5 Releases from Other Applications

The Japanese authorities have published information on the releases of hydrazine from a range of industries in 2001. This is summarised in **Table 5.2**. The report does not explain in detail how and why such releases from these industry sectors arise; it is possible however that it may relate to the use of steam and the consequent use of hydrazine hydrate as a corrosion inhibitor in boiler feedwater.

Table 5.2: Releases and Transfer of Hydrazine to Japanese Environmental Media (t/y) – 2001									
Industrios		Ву	Notifica	ation ¹		Notific	cation Exe		
		Release		Transfer		Release (estimated) ²			Total release
	Air	Water	Land	Sewer	Wastes	Air	Water	Land	
Electrical machinery and appliances	<0.5	1	0	0	<0.5	19	63	0	84
Waste disposal business	0	0	0	0	0	8	27	0	35
Chemical and allied products	2	9	0	1	113	5	15	0	31
Textile mill products	0	<0.5	0	0	0	6	19	0	25
Machine repair shops	-	-	-	-	-	3	10	0	13
Transportation equipment	-	-	-	-	-	3	9	0	11
Petroleum and coal products	0	<0.5	0	0	0	3	9	0	11
Ceramic, stone and clay products	-	-	-	-	-	3	8	0	11
Lumber and wood products	-	-	-	-	-	2	7	0	10

In duraturian		By Notification ¹ Notification I				cation Exe	Exempted		
industries		Release		e Transfer		Release (estimated) ²			Total release
	Air	Water	Land	Sewer	Wastes	Air	Water	Land	
Other ³	1	<0.5	0	1	94	12	38	0	51
Total ⁴	3	11	0	1	208	63	205	0	282
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5.2 Releases to the Working Environment

5.2.1 Dilution and Distribution of Hydrazine Hydrate

5.2.1.1 Information from Synthesis

Information on the patterns of exposure of UK workers to hydrazine as a result of the dilution of concentrates into weaker solutions for further distribution was published by the UK Health & Safety Executive in 2006. The available data are shown in **Table 5.3**.

Table 5.3: Patterns of Occupational Exposure to Hydrazine during Supply and Distribution of Hydrazine Hydrate – UK, 2006						
	Potentially exposed		Exposure events			
Work activity	population	Frequency (events/wk)	Number/ event	Event duration (mins)		
Bulk transfer (site 1)	3	3	1	180		
Bulk transfer (site 2)	3	1	1	30		

QC sample (site 1)	3	3	1	<5
Source: HSE (2006)				

The next table (**Table 5.4**) shows the available information on the exposure of workers at the two UK plants that were active in 2006. It should be noted that one of the two plants might no longer handle hydrazine. Moreover, the site operating with an open system in 2006 has since transformed into a closed system installation; hence, the data shown in the table overestimate current levels of exposure (these are assumed by a key consultee to be negligible, if any at all).

Site ID	Transfer system	Exposure duration (minutes)	Measured exposure (mg/m ³)	Equivalent 8 hour TWA (mg/m ³)*
Site 1 – visit 1	Open, manual	ca. 45	0.0045	0.00042
Site 1 – visit 2	Open manual	ca. 60	0.0096	0.00119
Site 1 – visit 3	Open, manual	41	0.013	0.00111
Site 2 – task 1	Closed, manual	15	0.002	0.00006
Site 2 – task 2	Closed, manual	15	0.003	0.00009
Source: HSE (2	006)			

A distributor of hydrazine hydrate offers a wide variety of packaging: 25 L polycans, 200 L drums, 500 L and 1,000 L IBCs²⁸. All containers are fitted with a closed system (Micromatic valves) which reduces operator exposure to hydrazine. The company in question also offers hydrazine solutions in a 30,000 litre road tanker. This is essential for users of dilute hydrazine hydrate to cope efficiently with the increased volumes of liquid being handled (Lansdowne Chemicals, 2010b).

5.2.1.2 Modelled Exposure

For illustrative purposes, we have estimated the potential inhalation and dermal exposure to hydrazine hydrate during pumping and tank transfer. It is assumed that dilution of hydrazine hydrate to weaker solutions is undertaken by a small number of companies in the EU and is conducted in a closed system (based on consultation findings). Annex 1 to this report presents the assumptions made in the estimates and how the Advanced REACH Tool (ART) and the ECETOC TRA v2 models have been used to derive the estimates. **Table 5.5** summarises the results.

²⁸ Intermediate bulk containers.

Table 5.5: Modelled Estimates for Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous Hydrazine) – Use in Closed Systems (100% solutions)

Parameter \ situation	Pumping hydrazine hydrate from drum	Tanker transfer – hydrazine hydrate
	100%	100%
Estimated inhalation exposure (mg/m^3)		
Fraction in product (%) [*]	64	64
Duration of activity (min)	15	180
75 th percentile during task – no RPE	0.29	0.87
Interquartile range during task – no RPE	0.15 - 0.58	0.44 – 1.7
Reasonable worst-case task – with RPE (90% reduction)	0.058	0.17
Reasonable worst-case full shift – no RPE during task	0.018	0.64
Reasonable worst-case full shift – with RPE during task	0.002	0.064
Estimated dermal exposure (mg/kg bw/day)	I	
Exposure to hydrazine – without PPE	4.39	4.39
Exposure to hydrazine – with PPE	0.44	0.44
Source: TNO calculations	I	1

5.2.2 Use in Water Treatment

5.2.2.1 Information from Literature

IARC (1999) suggests that exposure during the use of hydrazine in water treatment applications may occur. WHO (1987) further notes that, contrary to exposure during aerospace applications (where anhydrous hydrazine is used), workers at plants using high-pressure boilers are potentially exposed to relatively dilute solutions of hydrazine. This is confirmed by consultation.

ATSDR (1997) reports that long-term concentrations in areas where hydrazine was added to the boiler systems have been found in past research to generally lie below 0.1 ppm (0.13 mg/m^3), but short-term concentrations ranged up to 0.23 ppm (0.30 mg/m^3).

Information on the exposure of UK workers to hydrazine as a result of the use of its solutions in boilers of UK power stations is provided by HSE. The available data are for the year 2006 and are shown in **Table 5.6**.

Table 5.6: Patterns of Occupational Exposure to Hydrazine during the Use of Hydrazine Hydrate in Power Stations (estimated 90 sites) – UK, 2006					
	Potentially exposed		Exposure events		
Work activity	population	Frequency (events/week)	Number/event	Event duration (mins)	
Bulk transfer	1,800	90	1	15	
Source: HSE (2006)					

5.2.2.2 Consultation Findings

Table 5.7 summarises the responses we received through consultation in relation to worker exposure to hydrazine hydrate when its solutions are used to prevent corrosion. The consensus is that exposure of workers is likely to be very low, if any at all.

Additional information has been provided by a small number of companies that have asked for their input to be handled as confidential. This is presented in Confidential Annex 3.

Table 5.7: Consu Treatment	ltation Results on Worker Exposure from Use of Hydrazine Hydrate in Water
Company responding	Details of worker exposure
Company 19	A water treatment contractor. Employees use face covering filter masks (filter K) when handling hydrazine
Company 57	A nuclear power station contractor using hydrazine hydrate solutions as an oxygen scavenger. Activities potentially relevant to exposure include weighing and dilution with demineralised water (under ventilated hood) and pouring into air- tight circuits. No other protection is offered to operators. For up to 10 employees, exposure (by inhalation) has reportedly been measured and was found to be nil
Company 44	A nuclear power station contractor. Worker exposure may arise for up to ten employees during the transfer of hydrazine from the container in which it is delivered into storage tankers. Routes of exposure include inhalation and skin contact and employees use chemical gloves, respirators, chemical suites and chemical boots in the presence of local exhaust ventilation. Measured exposure levels have been found to be lower than 0.1 mg/m ³ (measurements undertaken and documented by a third party)
Company 11	A paper mill. When hydrazine was used in the past, numerous tests and measurements were performed to detect possible exposure. In this paper mill, no trace of hydrazine was ever found
Company 8	A boiler manufacturer. The company believes that the use of hydrazine hydrate may result in very little risk to workers due to the conditions of use and the equipment used for the transfer and dosing of the hydrazine hydrate solutions. Solutions are conditioned in closed plastic bottles which may be used for pumping and injecting in the water cycle. The suction element of the injection pumps can be fitted directly onto the hydrazine bottles. In case the hydrazine is transferred first in a larger size permanent plastic tank, adequate transfer pump is used without excessive and dangerous manipulation
Source: Consultat	ion

5.2.2.3 Modelled Exposure

For illustrative purposes, we have estimated the potential inhalation and dermal exposure to hydrazine hydrate during pumping and tank transfer associated with the preparation and dosing of hydrazine hydrate. According to consultation findings, companies may use hydrazine hydrate solutions in concentrations that range between 55% to ca. 5% (occasionally starting from a more concentrated solution and diluting this on-site before dosing). Annex 1 to this report presents the assumptions made in the estimates and how the ART and the ECETOC TRA v2 models have been used to derive the estimates. **Table 5.8** summarises the results.

Table 5.8: Modelled Estimates for Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous Hydrazine) – Use in Closed Systems (55% and 5% solutions)

und e / v solutions)				
Parameter \ situation	Pumping hydrazine hydrate from drum		Tanker transfer – hydrazine hydrate	
	55%	5%	55%	5%
Estimated inhalation exposure (mg/m^3)		I	_	
Fraction in product (%) [*]	35	3	35	3
Duration of activity (min)	1	5	18	0
75 th percentile during task – no RPE	0.16	0.014	0.48	0.041
Interquartile range during task – no RPE	0.081 - 0.32	0.007 – 0.027	0.24 - 0.95	0.021 - 0.082
Reasonable worst-case task – with RPE (90% reduction)	0.032	0.003	0.095	0.008
Reasonable worst-case full shift – no RPE during task	0.010	0.001	0.36	0.031
Reasonable worst-case full shift – with RPE during task	0.001	< 0.001	0.036	0.003
Estimated dermal exposure (mg/kg bw/day)				
Exposure to hydrazine – without PPE	2.40	0.21	2.40	0.21
Exposure to hydrazine – with PPE	0.24	0.021	0.24	0.021
Source: TNO calculations				

5.2.3 Use as a Reducing Agent for Metals

5.2.3.1 Information from Literature

No specific information has been identified.

5.2.3.2 Consultation Findings

Production of Precious Metals

Company 31 uses a very small amount of hydrazine in the recovery of precious metals and reports no exposure of workers to the substance.

Additional information submitted by other companies in this sector is presented in Confidential Annex 3.

Production of Basic Metals

Company 27 has provided some general information on the exposure of its workers to hydrazine during its use as a reducing agent for the removal of selenium from process liquids. This is reproduced in **Table 5.9**.

Table 5.9: Estimated Occupational Exposure to Hydrazine during its Use in theProduction of Basic Metals (Selenium Process, Finland, Company 27)					
Activity	Relevant process step	Route of exposure	Occupational exposure level	Exposure control measures	Number of exposed
Selenium removal process	Feeding to the reactor tank (closed system) Process fumes (closed process)	Inhalation	No data. Avoiding exposu PPE and LEV. PPE including gloves, butyl rubber or nit according to EN 374; (b) 1 ABEK-P3 (for protection particulates); (c) acid protection (d) chemical safety glasses	re by using appropriate des (a) gloves: chemical rile rubber category III respirators: filter from gases and f working clothing; and s	5
Source: Co	onsultation				

5.2.3.3 Modelled Exposure

Exposure during Electroless Plating

We have assumed that electroless plating is taking place in open systems (baths). Based on the available information, we have made assumptions on the concentration of hydrazine hydrate in the make-up solution and in the bath during operation. To capture a range of different concentrations of hydrazine in the bath (and to account for the diverse information collected during the study), we have assumed that the concentration of hydrazine may be 2% or 0.01%.

Annex 1 to this report presents the assumptions made in the estimates and how the ART and the ECETOC TRA v2 models have been used to derive the estimates. **Table 5.10** summarises the results.

Table 5.10: Estimated Inhalation and Dermal Exposure to Hydrazine (expressed as Anhydrous Hydrazine) – Preparation and Use of Electroless Plating Baths (open systems)				
Parameter \ situation	Preparation of bath	Operation of bath (2%)	Operation of bath (0.01%)	
Estimated inhalation exposure (mg/m ³)				
Fraction in product (%)	3	2	0.01	

Parameter \ situation	Preparation of bath	Operation of bath (2%)	Operation of bath (0.01%)
Duration of activity (min)	15	43	80
75 th percentile during task – no RPE	0.68	0.85	0.004
Interquartile range during task – no RPE	0.35 – 1.4	0.43 – 1.7	0.002 - 0.009
Reasonable worst case task – with RPE (90% reduction)	0.14	0.17	< 0.001
Reasonable worst case full shift – no RPE during task	0.044	1.7	0.009
Reasonable worst case full shift – with RPE during task	< 0.001	0.17	< 0.001
Estimated dermal exposure (mg/kg bw/da	y)		
Exposure to hydrazine – without PPE	4.46	0.006	< 0.001
Exposure to hydrazine – with PPE	0.45	< 0.001	< 0.001

Exposure during Metals Production

The assumptions made for this area of hydrazine hydrate applications are identical to those made for closed systems (e.g. water treatment). The reader is referred to **Table 5.8** which provides the relevant estimates for inhalation and dermal exposure.

5.2.4 Use in Aerospace Applications

5.2.4.1 Information from Literature

Exposure to hydrazine is expected to occur amongst aerospace workers. In 1999, Ritz *et al* concluded that occupational exposure to hydrazine or other chemicals associated with rocketengine testing jobs increased the risk of dying from lung cancer, and possibly other cancers, in a population of aerospace workers. A later study by Ritz and colleagues (Ritz *et al*, 2006) confirmed that exposure to hydrazine increases the risk of lung cancer and colon cancers. Results for other cancer sites were inconclusive.

Boice *et al* (2006) refers to exposure to hydrazines, predominantly MMH, during small engine tests (in the years 1961 to 1999). In the dataset considered in this journal article, it was found that, for relatively short periods of time and for a few limited engine programs, a small number of workers were potentially exposed to hydrazines at several large engine testing areas.

Exposure to workers may occur during loading or unloading of propellants, transfer operations, or testing of spacecraft components that use hydrazine fuels, according to Fajen & McCammon (1988). Back in 1987, WHO noted that workers normally exposed to anhydrous or concentrated

hydrazine were provided with respiratory and skin protection²⁹. The difference between air levels outside and inside protective masks was illustrated by Cook *et al* (1979) who found levels of 0.29-2.59 mg/m³ outside the masks at a rocket propellant-handling facility, and levels below the detection limit of 0.013 mg/m³ inside the masks. Evaporation of hydrazine from a liquid spill can be sufficient to generate an atmospheric concentration as high as 4 mg/m³ (WHO, 1987b) and much higher levels (800 mg/m³) have been observed at the site of a leak (Suggs *et al*, 1980). Therefore, workers in facilities where exposure to these chemicals is possible are required to wear protective respirators.

Indeed, this is currently the case in the EU aerospace industry; an example of the type of apparatus used by crews fuelling satellites with hydrazine propellant can be found on the European Space Agency's Internet site³⁰.

Some information on measured levels of hydrazine in the working environment associated with aerospace applications is provided by WHO in a 1987 publication and is reproduced in **Table 5.11**.

Site	Approximate numbers exposed Measured		evels (mg/m ³)	
	Normal	Potential	Normal	Exceptiona
Rocket testing	10	100	0.01-0.02	0.14*
Source: WHO (1987	10	100	0.01-0.02	0.

5.2.4.2 Consultation Findings

Companies that play a leading role in the EU aerospace industry sector have provided some information which is presented in Confidential Annex 3. On the other hand, **Company 25** has also provided non-confidential data on occupational exposure to hydrazine during its use in the manufacture of thrusters. These are reproduced in **Table 5.12**.

Table 5.12: Measured Occupational Exposure during the Use of AnhydrousHydrazine in the Manufacture of Thrusters (Company 25)					
Activity	Relevant process step	Route of exposure	Occupational exposure level	Exposure control measures	Number of employees exposed
Deconta - mination	Cleaning of equipment	Inhalation (vapour in air)	Nil	Yes (unspecified)	3
Source: C	onsultation				

²⁹ ATSDR (1997) suggests that full-body supplied-air suits are usually worn during these operations.

³⁰ Available here: <u>http://www.esa.int/esaCP/SEMPJQ9KF6G_index_1.html</u>.

5.2.4.3 Modelled Exposure

Estimates for inhalation and dermal exposure have been made with the ART and ECETOC TRA v2 models. It has been assumed that the product handled is 100% anhydrous hydrazine. It is also assumed that the reduction in exposure afforded by PPE is 90%. However, it is recognised that, especially where filling of satellites with propellant takes place, with more advanced RPE, such as equipment with an independent air supply, higher reduction effects can be achieved. For powered filtering devices incorporating helmets or hoods³¹, a reduction of 97.5% can be assumed (i.e. an assigned protection factor of 40, Brouwer *et al*, 2001). This would lead to exposure levels that are four times lower than those calculated with a reduction effect of 90%.

Annex 1 to this report presents the assumptions made in the estimates and how the ART and the ECETOC TRA v2 models have been used to derive the estimates. **Table 5.13** summarises the results.

Parameter \ situation	Pumping from drum – anhydrous (>99%)
Estimated inhalation exposure (mg/m ³)	
Fraction in product (%)	100
Duration of activity (min)	15
75 th percentile during task – no RPE	0.46
Interquartile range during task – no RPE	0.23 - 0.90
Reasonable worst case task – with RPE (90% reduction)	0.09
Reasonable worst case full shift – no RPE during task	0.028
Reasonable worst case full shift – with RPE during task	0.003
Estimated dermal exposure (mg/kg bw/day)	
Exposure to hydrazine – without PPE	6.86
Exposure to hydrazine – with PPE	0.69

5.2.5 Use in Defence Applications

5.2.5.1 Information from Literature

Fighter Jet Emergency Power Units

³¹ SCAPE (Self-contained Atmospheric Protective Ensemble) suits.

A rather dated source (Christensen, 1978) discusses the exposure of workers to hydrazine during maintenance operations associated with the F-16 fighter jet EPU. During the week of 23 to 27 January 1978, a survey team from the US Air Force Occupational and Environmental Health Laboratory identified the following tasks as potentially relevant to worker exposure to hydrazine: nitrogen depressurisation, catalyst purge, poppet valve replacement and the entire refilling procedure. Measurements indicated compliance with the then Time Weighted Average limit value of 0.1 ppm (0.13 mg/m³) hydrazine; however, potential peak exposures which ranged as high as 5 to 8 ppm (6.6 to 10.5 mg/m³) occurred during some tasks. A technician would be unaware of many such exposures since concentrations below the odour threshold of 3 to 5 ppm (3.9-6.6 mg/m³) give no warning.

Some information on measured levels of hydrazine in the working environment associated with the use of the substance in fighter jets is provided by WHO in a 1987 publication and is reproduced in **Table 5.14**.

Table 5.14: Occupational Exposure to Hydrazine in the USA – Fighter Jet Applications (1986)				
Site	Approximate n	Approximate numbers exposed		vels (mg/m ³)
	Normal	Potential	Normal	Exceptional
F-16 fighter station	32		-	0.04-0.05
Source: WHO (1987))			

The US Department of Defense (1999) provides information on safety and engineering measures that should be taken to prevent release and exposure of hydrazine from the handling of hydrazine-based propellant for F-16 fighter jets. This handbook requires, among others, the following measures to be taken:

- provision of vapour sniffers for use in the H-70 fuel drum storage area and servicing area to alert personnel to excessive levels of H-70 fuel vapours. These should be capable of detecting 10 ppb of H-70;
- provision of a facility respirator air system (recommended);
- provision of an explosion proof observation window between the H-70 fuel drum storage area and the tank servicing area;
- segregation of mechanical ventilation for regulated versus non-regulated areas;
- design of ventilation systems for regulated areas to maintain a negative pressure of 12 to 25 Pa with respect to adjacent non-regulated areas;
- design of ventilation for servicing and storage areas to provide a minimum of 20 air changes per hour;
- design of the ventilation system for automatic shutdown in the event of a fire within the facility; and
- use of flexible exhaust vent of the "elephant trunk" type to exhaust vapours that are released when full hydrazine drums are opened. Design for airflow at the vent nozzle to be approximately 71 L/s.

All personnel assigned to the hydrazine response team (HRT) on a relevant air force base have access to a complete set of protective ensemble for hydrazine protection (US Air Force, 2010):

- during emergency response, after Fire Department confirmation of hydrazine, Level-A equipment will be required. This equipment consists of boots, gloves, Self-contained Breathing Apparatus (SCBA) and totally encapsulated vapour tight suit³²;
- during EPU disconnects, EPU purge, spill containment, or clean-up, Level-A or B equipment will be required, if hydrazine is noted;
- during disconnect of a fired EPU, SCBA respiratory protection is required;
- all maintenance performed inside the hydrazine facility will require the use of level-A or level-B equipment, if hydrazine is suspected or confirmed; and
- during hydrazine storage facility inspection, personnel will be required to wear at a minimum: gloves, apron and an in-line supplied air respirator or assure the ventilation is adequate by opening at least two doors for cross-ventilation.

Submarine Rescue System Gas Generators

No information has been identified in the open literature.

5.2.5.2 Consultation Findings

Fighter Jet Emergency Power Units

No information has been obtained through consultation.

Submarine Rescue System Gas Generators

Company 14 which uses hydrazine hydrate for the manufacturer of these gas generators also uses the substance in aerospace applications. Therefore, information that has been provided in relation to aerospace uses of hydrazine hydrate (and is presented in Confidential Annex 3) should, to an extent at least, cover operations relating to the manufacture of submarine rescue systems.

5.2.5.3 Modelled Exposure

Estimates of inhalation and dermal exposure are largely based on the assumptions made for aerospace uses, as detailed in Annex 1 to this report. The key difference is that it is assumed that the propellant used in the EPU has a 70% hydrazine concentration. The comment on the use of higher specification PPE (with a removal rate of 97.5%) made in Section 5.2.4 would also apply. **Table 5.15** summarises the results.

³² Pictures of typical PPE used by the US Air Force and the Royal Netherlands Air Force are available at <u>http://www.169fw.ang.af.mil/shared/media/photodb/photos/081212-F-0675P-017.jpg</u> and <u>http://attach.high-g.net/attachments/dscf4336_169.jpg</u>.

Parameter \ situation	Pumping from drum – anhydrous (70%)
Estimated inhalation exposure (mg/m ³)	
Fraction in product (%)	70 (option 'main component' used in ART)
Duration of activity (min)	15
75 th percentile during task – no RPE	0.32
Interquartile range during task – no RPE	0.16 - 0.64
Reasonable worst case task – with RPE (90% reduction)	0.064
Reasonable worst case full shift - no RPE during task	0.020
Reasonable worst case full shift – with RPE during task	0.002
Estimated dermal exposure (mg/kg bw/day)	
Exposure to hydrazine - without PPE	4.80
Exposure to hydrazine - with PPE	0.48

Table 5.15: Modelled Estimates for Inhalation and Dermal Exposure to

It is assumed that exposure associated with the handling of anhydrous hydrazine in the manufacture and servicing of gas generators for submarine rescue systems will fall between the ranges indicated by the estimates for aerospace applications and those presented in **Table 5.15**.

6 CURRENT KNOWLEDGE ON ALTERNATIVES

6.1 Alternatives for Water Treatment

6.1.1 Availability and Identities/Description of Alternatives

6.1.1.1 Alternative Substances

Alternative substances that have been identified in literature and suggested by consultees include those shown in **Table 6.1**.

Table 6.1: Overview of Alternative Corrosion Inhibitors (Substances)			
Substance name	Formula	EC Number	CAS Number
Sodium sulphite	Na ₂ SO ₃	231-821-4	7757-83-7
Sodium dithionite	$Na_2S_2O_4$	231-890-0	7775-14-6

ANNEX XV - IDENTIFICATION OF HYDRAZINE AS SVHC

Carbohydrazide	H ₂ N-NH-C(O)-NH-NH ₂	207-837-2	497-18-7
Diethyl hydroxylamine (DEHA)	(CH ₃ CH ₂) ₂ NOH	223-055-4	3710-84-7
Methyl ethyl ketoxime (MEKO)	H ₃ C-C(NOH)-C ₂ H ₅	202-496-6	96-29-7
Hydroquinone	HO-C ₆ H ₄ -OH	204-617-8	123-31-9
Tannins Tannic acid 	C ₇₆ H ₅₂ O ₄₆	215-753-2	1401-55-4
Filming amines			
 isopropyl hydroxylamine 	(CH ₃) ₂ CHNH(OH)	264-968-8	5080-22-8
 (IPHA) octadecylamine (ODA) 1-amino-4- methylpiperazine 8-azaguanine 	$C_{18}H_{37}NH_2$	204-695-3	124-30-1
	$C_5H_{13}N_3$	230-053-7	6928-85-4
	$C_4H_4N_6O$	205-148-1	134-58-7
Ascorbic acid derivatives			
sodium erythorbate	C ₆ H ₇ NaO ₆	228-973-9	6381-77-7
ascorbic acid	$C_6H_8O_6$	200-066-2	51-81-7
Oxalates			
• ammonium oxalate	NH ₄ O(O)CC(O)ONH ₄	214-202-3	1113-38-8
oxalic acid	HO(O)CC(O)OH	205-634-3	144-62-7
Formic acid	НСООН	200-579-1	64-18-6
Hydrogen	H ₂	215-605-7	1333-74-0
Source: Literature and Consulta	ntion		

Sodium sulphite: sodium sulphite reacts chemically with dissolved oxygen, producing sodium sulphate (Guardian CSC, undated). The rate of reaction between sodium sulphite and oxygen is quite rapid at temperatures near and above the normal boiling point of water. When necessary, the speed of this reaction can be accelerated considerably by using a trace amount of transition metal as a cobalt salt. The sodium sulphite reactions are (Guardian CSC, undated):

Uncatalysed:

$$2 \operatorname{Na_2SO_3} + \operatorname{O_2} \rightarrow 2 \operatorname{Na_2SO_4}$$

Catalysed:

$$O_2 + 6 CoSO_4 + 2 H_2O \rightarrow 2 Co_2(SO_4)_3 + 2 Co(OH)_2$$

$$Co_2(SO_4)_3 + Co(OH)_2 + Na_2SO_3 \rightarrow Na_2SO_4 + 3 CoSO_4 + H_2O$$

Sodium sulphite is promoted as the fastest and the least expensive oxygen scavenger available in the marketplace; however, it offers no passivation, it is not volatile enough to protect the condensate loop, and it builds up sulphate salts in the boiler system (Arkema, 2003). In addition, other boiler water chemicals are alkaline in nature and when they are mixed with catalysed sodium sulphite, the alkalinity reacts and causes the cobalt sulphate catalyst to drop out (Guardian SCS, undated).

The use of sodium sulphite is generally limited to about 900 psi (62 bar), beyond which it could decompose to sulphur dioxide and hydrogen sulphide. Furthermore, sodium sulphite is not used in high-pressure applications such as electricity generation, where it can foul turbines (Arkema, 2003). Advantages to the use of sulphite are that the higher the feedwater temperature the less sulphite is required, its low cost and the fact that it is a colourless product (Accepta, 2010b).

The stoichiometry of the reaction shows that 7.88 ppm of sodium sulphite would be required to combine with 1 ppm of oxygen (Guardian CSC, undated).

Sodium dithionite: BAuA (1991) mentions sodium dithionite as a potential alternative. No further information is available.

Carbohydrazide: this is a hydrazine substitute designed to act like hydrazine but does not have the same hazard profile as hydrazine. It does not contribute to the boiler solids and reacts at a rate of 1.4 ppm of carbohydrazide for every 1 ppm of oxygen. This, however, will also form an additional 0.7 ppm of CO₂, which will have to be taken into account when calculating the neutralising amine requirement³³, as CO₂ contributes to carbonic acid formulation in the return lines:

$$H_6N_4CO + 2O_2 \rightarrow CO_2 + 2N_2 + 3H_2O$$

Carbohydrazide directly reacts with oxygen at low temperatures and pressures. In addition, at a temperature above 180°C, carbohydrazide will break down to form hydrazine (B&V Group, 2010).

Reportedly, carbohydrazide can be used in boilers of any pressure, up to and including 3,200 psi (220 bar) (Accepta, 2010c). Its use in low-pressure boilers may be restrained by its relatively high cost (B&V Group, 2010). Carbohydrazide is available as a buff coloured powder, but for boiler applications, it can be supplied as an aqueous solution. A low solubility limits the strength of the products available and slightly more concentrated products can be supplied to hot regions. Notably, carbohydrazide cannot be used where the steam will come into contact with food (B&V Group, 2010).

Diethyl Hydroxylamine (DEHA): DEHA is a volatile oxygen scavenger, which is usually sold as an 85% or 25% liquid. It has the ability to passivate the metal surfaces in the boiler, then pass out of the boiler with the steam, and act as a metal passivating agent in a similar fashion to

 $^{^{33}}$ CO₂, when dissolved in the condensate as carbonic acid, H₂CO₃, results in corrosion in the return line (Arkema, 2001). Neutralising amines are steam volatile alkaline materials which prevent corrosion caused by CO₂. The amines react with carbonic acid to form amine carbonates or bicarbonates and fix CO₂. The elevation of pH to >8.5 minimises the corrosion rate. The three most commonly used neutralising amines are morpholine, diethyleminoethanal (DEAE) and cyclohexylamine. Neutralising amines cannot protect against oxygen attack.

hydrazine (Guardian CSC, undated). It is claimed that DEHA provides good passivation, high volatility, low toxicity, and good thermal stability (Arkema, 2003).

When reacting with oxygen, DEHA does not lead to any solid residues, but will give organic acids. Typically, the reaction product would be acetate, nitrogen and water.

4 (CH₃CH₂)₂NOH + 9 O₂
$$\rightarrow$$
 8 CH₃COOH + 2 N₂ + 6 H₂O

Acetic acid is neutralised to acetate in the boiler and then eventually breaks down into carbon dioxide. This must be taken into account when reviewing the neutralising amine programme. Some decomposition of DEHA into ammonia may occur; however this does not occur until temperature reaches 280°C, a temperature higher than the one at which hydrazine's breakdown to ammonia starts (Guardian CSC, undated).

DEHA finds use in high-pressure and supercritical boilers where any solids would present a severe problem (Arkema, 2003) and is promoted by some companies as the preferred alternative to hydrazine (B&V Group, 2010). A shortcoming of DEHA-based oxygen scavengers is the sluggish kinetics of oxygen capture in the feeding waters at low and medium temperatures. The usual remedy for this is the addition of co-scavengers, of which hydroquinone is a frequently used one (but note that catalysts may be used in hydrazine hydrate solutions too) (Hater & Schweinsberg, undated). Copper salts may also be used to catalyse the reactions of DEHA (Guardian CSC, undated).

In theory, 1.24 ppm DEHA is required to remove 1 ppm oxygen. In practice, however, 3 ppm DEHA is recommended for most boilers at operating conditions (DEHA replaces hydrazine at a 1.2:1.0 ratio) (Arkema, 2003).

Methyl Ethyl Ketoxime (MEKO): MEKO is a volatile oxygen scavenger, which has a higher distribution ratio than DEHA. This allows it to operate more effectively in long-run condensate systems than DEHA. Its reaction with oxygen gives methyl ethyl ketone, nitrous oxide and water (Arkema, 2001):

 $2 \text{ H}_3\text{C-C(NOH)-C}_2\text{H}_5 + \text{O}_2 \rightarrow 2 \text{ H}_3\text{C-C(O)-C}_2\text{H}_5 + \text{N}_2\text{O} + \text{H}_2\text{O}$

MEKO does not have the passivation performance of DEHA or hydrazine (Guardian CSC, undated), although some passivation capabilities are present (Arkema, 2001).

MEKO may be fed neat from a 100% solution to the feed water system at a rate of 5.4 ppm of MEKO for every 1 ppm of oxygen.

Hydroquinone: hydroquinone may be used as a catalyst for hydrazine, DEHA, and carbohydrazide. However, it also is capable of acting as a standalone oxygen scavenger. It has very rapid reaction rate, even in relatively cold water. This ability enhances the performance of the products in which it is used as a catalyst allowing them to perform in low-pressure systems.

Hydroquinone is fed at a rate of 6.9 ppm of hydroquinone to 1 ppm of oxygen (Guardian CSC, undated).

Tannins: tannins are typically used in blends. BAuA (1991) refers to CAS Number 1401-55-4 (for tannic acid) as relevant in this context. No further information on their performance is available.

Filming amines: these create an oil-attractive, water-repellent film on metal surfaces which is resistant to both carbon dioxide and oxygen (Spirax-Sarco, 2010). Treatment with filming

polyamines is based on the combination of several actions (BKG Water Solutions, 2010): (a) formation of a mono-molecular film, adsorbed on metal surfaces all over the system; (b) dispersion of scale-forming salts; and (c) pH control by means of neutralising amines. The protective film barrier is continuously being removed (a little at a time), requiring continuous feeding of the filming amine based on steam flow rather than feedwater alkalinity. The formation of gunk balls (gunking) can occur due to overfeed, contaminants in the condensate or wide pH swings causing deposits to form in low flow areas like steam traps. The neutralising amines, although they will elevate pH, they also act to provide a better distribution of the filming amine throughout the condensate system, which in turn helps to prevent gunking (Water Services Ltd, 2010).

Ascorbic acid derivatives: liquid oxygen scavengers based on sodium erythorbate (isoascorbic acid, sodium salt) (possibly in mixtures with neutralising amines) can be used in boilers where the steam comes into contact with food or food products (as long as the neutralising amine is less than 15ppm in the condense (B&V Group, 2010)). It can be used in boiler plants operating up to 580 psi (40 bar); erythorbate is a very strong passivating agent for iron (Guardian CSC, undated).

The feed rate of 10% erythorbate acid is 11 ppm of the acid for every 1 ppm of oxygen (Guardian CSC, undated).

Table 6.2: Reaction and Breakdown Products of Selected Alternative Oxygen Scavengers			
Chemical/Formula	% C (wt.)	Reaction and/or breakdown products	
Hydrazine	0	Nitrogen, water, ammonia	
Carbohydrazide	13.3	Hydrazine, nitrogen, water, ammonia, carbon dioxide	
DEHA	53.9	Acetaldehyde, acetic acid, dialkylamines, ammonia, nitrate, nitrite	
МЕКО	55.2	Methyl ethyl ketone, hydroxylamine, nitrogen, nitrous oxide, ammonia, carbon dioxide	
Erythorbic acid	40.9	Dihydroascorbic acid, salts of lactic and glycolic acid, carbon dioxide	
Hydroquinone	65.5	Benzoquinone, light alcohols, ketones, low molecular weight species, carbon dioxide	
Source: Anonymous (2008)			

Table 6.2 presents in more detail the reaction and/or breakdown products of the key alternative oxygen scavengers.

6.1.1.2 Comparison of Alternative Substances

 Table 6.3 presents a quick overview of some key features of selected oxygen scavengers discussed above.

Table 6.3: Comparison of Key Properties of the Main Oxygen Scavenger Substances					
Scavenger	Volatile	Contributes	Hazar-	Flammable/	Theoretical

		Solids	CO ₂	Organics	dous?	Combustible	Dosage
Hydrazine	Yes	No	No	No	Yes	No*	1:1
Carbohydrazide	Yes	No	Yes	No	No**	No	1.4:1
Sodium Sulphite	No	Yes	No	No	No	No	8:1
DEHA	Yes	No	Yes	Yes	Yes	F	1.2:1
МЕКО	Yes	No	Yes	Yes	Yes	С	5.4:1
Erythorbate	No	No	Yes	Yes	No	No	11:1
Hydroquinone	No	No	Yes	Yes	No***	No	6.9:1

Source: based on Arch (2010k)

* although anhydrous hydrazine has a Flammable classification, here the substance is used in its hydrated form and typically in highly diluted conditions

** breaks down to hydrazine at high temperatures

*** dangerous for the environment

A comparison of the oxygen removal capability of different corrosion inhibitors is given in a paper prepared by the Environmental Research Institute of the University of Connecticut in collaboration with the US supplier of hydrazine Arch Chemicals (Huang *et al*, undated).

Huang et al investigated the removal rates of dissolved oxygen by nine oxygen scavengers by injecting a certain amount of scavenger solution into a 300 ml oxygen-saturated solution at 2°C. The results of the tests showed that the dissolved oxygen was rapidly removed by hydroquinone and catalysed hydrazine hydrate solutions. The results also indicated that dissolved oxygen was efficiently removed by other four chemicals, sodium sulphite, uncatalysed hydrazine, isoascorbic acid, and DEHA, although the removal rates were not as fast as those of hydroquinone/catalysed hydrazine. The reaction of dissolved oxygen with carbohydrazide was relatively slow and oxygen depletion could not be achieved within a reaction period of 30 minutes. In addition, the dissolved oxygen concentration did not decrease with time after the injection of MEKO solution, which indicates that the reaction rate of oxygen with MEKO was extremely slow or even no reaction happened under the test conditions. The study concluded that, on a theoretical basis, only one kg of hydrazine is required to react with one kg of oxygen, whereas the other agents, because of their higher equivalent weights, must be dosed in higher amount regardless of the oxygen-scavenger reaction rate. This, combined with the cost of the chemicals, suggested that from both technical and economic aspects, hydrazine should be considered the oxygen scavenger of choice.

These results are not necessarily mirrored in other literature sources. For example, Anonymous (2008) suggests that carbohydrazide outperforms hydrazine by offering better passivation and faster oxygen scavenging at lower temperatures.

Finally, BAuA issued a technical analysis of alternatives to hydrazine for water treatment in 1991. At the time, ammonium ascorbate, sodium dithionite and sodium sulphite were found to be "*toxicologically recommended with minor limitations*", while the toxicological properties DEHA, MEKO and hydroquinone could not be fully assessed.

6.1.1.3 Alternative Techniques

BAuA (1991) suggests that the physical oxygen elimination by vacuum and pressure thermal deaeration could be sufficient and can be used in the place of chemical scavengers such as hydrazine. Such an approach is suggested to be feasible during continuous operation, but can be feasible with some limitations with intermittent operations (e.g. during start-ups of ventilated parts of the plant) (German Federal Institute for Occupational Safety and Health, 2010). Other possibilities include:

- catalytic reduction; and
- corrosion prevention without hydrazine, by addition of other chemicals (e.g. increase of pH by NH₃, NaOH, Na₃PO₄) as long as boiler water treatment systems are manufactured and run according to specified technical rules.

Information along similar lines has been received in the form of a completed questionnaire from a member of the European Power Plant Suppliers Association (**Company 8**). The company advised that use of hydrazine hydrate was normal practice in the past in order to eliminate any trace of dissolved oxygen in the deaerated water. Years ago, worldwide scientific literature illustrated corrosion problems associated with hydrazine, such as flow-accelerated corrosion (FAC). Key European contractors and operators of utility power plants were, allegedly, the first to stop continuous hydrazine injection in water cycle for new projects³⁴. For existing plants, changing a long-standing practice such as the use of hydrazine hydrate is a more problematic process.

For steam generators (power plants), modified water treatments and better water quality³⁵ can drastically reduce or even eliminate the use of hydrazine during permanent operation. Those two parameters (very high water quality (mainly very low acid conductivity) and slightly higher pH with volatile ammonia) are already common practice for utilities (power plants), the company suggests. Oxygen content in the water is no longer the leading parameter as far as the condenser works properly (without a leak).

In steam generator applications, long-term operating experiences exist already which have demonstrated the feasibility of alternatives without continuous hydrazine injection. The present market trend is to stop continuous injection of hydrazine but keep the injection system available to maintain some operating flexibility in case of emergency conditions, such as a leak in the condenser.

A relevant VGB³⁶ standard has recently been revised accordingly (VGB Powertech, 2004). The standard was prepared by a joint European technical committee with representatives from VGB, Fachverband für Dampfkessel-, Behälter- und Rohrleitungsbau (FDBR) and the European Power Plant Suppliers Association (EPPSA). It recommends, among others, changes such as those described above, i.e. (a) good control of the acid conductivity, (b) good control of the pH

³⁴ US and Asian players are moving later and more slowly towards this new practice.

³⁵ Water quality must be controlled and maintained at the highest level: demineralised water, high purity with low conductivity, adequate deaeration in condenser or deaerator, pH control with NH₃, etc.

³⁶ VGB PowerTech e.V., abbreviated VGB, is the European technical association for power and heat generation. See VGB's Internet site here: <u>http://www.vgb.org/en/vgb_powertech.html</u>.

by ammonia injection, (3) acceptance of a minimum of dissolved oxygen without adding any oxygen scavenger, which shall only be used if oxygen is no longer under control (for example, when a leak in the condenser occurs). The same concept has been studied and published upon by the US Electric Power Research Institute (EPRI) several years ago: EPRI has advised that FAC can be exacerbated by permanent and continuous injection of oxygen scavengers.

Finally, some further confidential information on alternatives techniques is provided in Confidential Annex 4, based on the experiences of **Company 26**.

6.1.2 Practical Experience of EU Stakeholders with Alternatives

The following paragraphs outline the experience of certain consultees with alternative corrosion inhibitors.

Company 32: this is an operator of power stations. In light of the hazard profile of hydrazine, **Company 32** has carried out an extensive study to compare the performance of potential alternatives to hydrazine under typical AGR plant operating conditions. A number of candidate chemical scavengers have been tested, namely:

- carbohydrazide;
- DEHA;
- IPHA; and
- hydrogen.

In all instances, these alternatives were found to be slow and/or ultimately degrade to form hydrazine (refers to carbohydrazide) or other undesirable by-products e.g. carbon dioxide. Furthermore, a number of these substances possess known technical limitations and require catalysts to facilitate their respective reactions. Of the alternatives tested, none removed oxygen from the boiler as efficiently as hydrazine. Alternative chemicals continue to be assessed but, to date, there are no known suitable alternatives essential in maintaining the safe operation of the plant, claims **Company 32**.

The company notes that the focus for the power industry has been on optimising the use of hydrazine to minimise any hazards since its continued use is considered to be the only viable option. In order to ensure health & safety risks are properly managed, the primary requirement is that the manual handling of the reagent is limited. The reagent is delivered in bulk containers with a preference for pre-diluted reagent where this is appropriate.

Company 22: this is an operator of combined heat and power plants. These use coal, natural gas, and fuel oil as alternate fuel. The company has used in the past carbohydrazide (5-10%) solutions, MEKO (30-50%) solutions and products based on amines (a product based on 8-azaguanine has been mentioned). The testing results showed that the oxygen removal abilities of these chemicals did not fulfil the demands of the water/steam generation process. The MEKO and amine products were found to increase the electrical conductivity of the water-steam cycle beyond what is prescribed for the plant in question. On the other hand, the carbohydrazide product decomposes to give hydrazine, as expected. The company notes that any experiment with alternative oxygen scavengers should last several months, so that the required chemical balance in the process and on metal surfaces can be achieved.

On the other hand, 15% solutions of hydrazine hydrate, which the company uses after diluting them down to 2%, can meet these requirements and are also accompanied by decades of experience. Therefore, the company is not currently working towards the replacement of

hydrazine. The company has obtained approval from its national authorities to use hydrazine, taking into account past studies for the replacement of hydrazine with less harmful chemicals. The company argues that hydrazine is used in a closed process and there should not be any exposure to it.

Company 19: this is a large company offering water treatment services across the EU. The company confirmed the current use of carbohydrazide as an oxygen scavenger for feedwater and for boiler start-up. Another alternative identified was hydroquinone which may essentially be used in similar applications. The company has claimed that carbohydrazide is used in all EU countries were hydrazine is "*not allowed*" (for example, in Scandinavia). On the other hand, hydroquinone is mainly used in USA and Canada (due to commercial reasons).

These alternatives already find use in water treatment projects around the world, according to the company. However, they may not replace hydrazine in all designs and all applications. Alternatives (other than carbohydrazide) result in the formation of organic acids which are problematic for the normal operation of the boiler, mainly as they affects the cation conductivity of steam and condensate. In high contents, organic acids may cause corrosion problems, mainly in steam turbines or other steam consuming equipment. Because of organic acids increase, not all alternatives are suitable for normal operation of well-closed circuits.

Company 8: this is a boiler maker specialising in combined cycle/heat recovery steam generator technology for utility and industrial power plants. The company is not a producer or direct user of hydrazine but advises end-users or prescribes the use of some chemicals for the adequate corrosion protection of its equipment (the company often has to produce water chemistry procedures or water specifications for the end users in order to define adequate corrosion protection of the boiler components). As shown earlier in this Section, the company would support the elimination of use of chemical oxygen scavengers, at least in new installations. The company confirmed that several known alternative oxygen scavengers are already in use and no additional time would be needed for their development.

Company 44: this is a water treatment contractor for the nuclear power industry (for the removal of solids). In the 1990s, the company tested substances such as ascorbic acid, oxalates and formic acid as alternative reducing agents (for the removal of solids from steam generators). The company claims to have met problems regarding the corrosion rate of the metal and the efficiency of the process when such alternatives were trialled.

Company 38: this is a supplier of hydrazine solutions to the power generation industry. The company suggests that the main alternative to hydrazine hydrate for boiler feed application is carbohydrazide. It notes that carbohydrazide may contain up to 100 ppm of hydrazine³⁷. Furthermore, the product may come in powder form and in order to dose it into boiler feed applications it would need to be diluted. This might lead to potential issues with exposure to dust. On the contrary, as hydrazine hydrate solutions are already in liquid form, it is relatively easy to create a 'close system' for dilution and dosing.

The company indicates that most of the power stations in the UK are reluctant to change from hydrazine hydrate to carbohydrazide due to issues with boiler feedwater quality when using carbohydrazide (high conductivity and poor performance). Hence, a significant majority of power stations still prefer to use hydrazine hydrate. Notably, UK power stations were supplied in the past with hydrazine hydrate 55% (35% when expressed as anhydrous hydrazine);

³⁷ The company referred us to this website: <u>http://carbohydrazide.net/</u>

however, hydrazine became a named substance under the Seveso II Directive³⁸, whereby if a company stored solution with a concentration above 5% and a volume above 2 metric tonnes, the site would become a Top Tier CoMAH site³⁹. This led to most of the stations taking a more dilute form of hydrazine, hydrazine hydrate 7.5% w/w (4.8% when expressed as anhydrous hydrazine).

Company 23: this is the German subsidiary of a Japanese company manufacturing oxygen scavengers. The company has developed an amine-based oxygen scavenger for boilers and has patented the product as a replacement for hydrazine. The patented oxygen scavenger contains a heterocyclic compound having N-substituted amino group such as 1-amino-4-methylpiperazine and a hydroxylamine compound such as DEHA. The oxygen scavenger may further contain a polyhydric phenol type catalyst such as pyrogallol to improve performance at low temperatures (Shimura & Takahashi, 2006).

The company claims to have experience using this new product in many boiler systems worldwide, both low- and high-pressure ones. In most cases, it is claimed that the boiler systems do not require any re-design or process changes to adapt to the new system. The company notes:

- there are certain control parameters, that differ from country to country, for example the level of cation conductivity in condensate;
- whilst in most applications of high-pressure boilers the product can maintain the operational specifications, sometimes an adjustment of dosing or other process adjustments might be necessary; and
- in some cases, an oxygen scavenging effect is requested for very low temperatures in feedwater lines. The reactivity of this amine-based product at low temperature is lower than the one of activated hydrazine hydrate solutions.

The company suggests that this technology does not require any further R&D as the product is already on the market. Many customers of the Japanese company located in Japan and the wider Pacific region currently use it; the uptake in the EU is still limited.

The reader is advised that some confidential information in Annex 4 reports on tests undertaken by a company using a product based on 1-amino-4-methylpiperazine. The Annex contains further information on the experiences of certain companies with alternative substances and techniques.

Finally, **Box 6.1** (overleaf) outlines the position of Union of the Electricity Industry – Eurelectric, which has been consulted for the purposes of this study.

³⁸ Directive 2003/105/EC of the European Parliament and of the Council of 16 December 2003 amended Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances (the Seveso II Directive). Following the amendment hydrazine (alongside other carcinogens) falls under the provisions of Articles 2 and 3 if it is stored at a concentration above 5% at more of 0.5 tonnes and under the provisions of Article 9 if it is stored at a concentration above 5% at more of 2 tonnes.

³⁹ UK Control of Major Accident Hazards Regulations, implementing the Seveso II Directive.

Box 6.1: (Abridged) Position of the Union of the Electricity Industry – Eurelectric (Eurelectric, 2010)

Hydrazine as Reagent of Choice - Importance of Operational Considerations

High-pressure steam generating plant operates with steam temperatures of $>450^{\circ}$ C. At these operating conditions, all candidates other than hydrazine decompose to undesirable products. Hydrazine has the particular advantage that its breakdown products are inert and therefore do not contribute to dissolved solids in the system.

The breakdown products produced by alternatives to hydrazine obscure normal monitoring parameters (primarily "After Cation" conductivity) so that hazardous operational conditions may be overlooked.

The organic breakdown products occurring as a result of the use of alternatives to hydrazine can be acidic or precursors of acid products. These can form corrosive solutions in early condensate on the turbine and can result in a pitting attack. This can progress to stress corrosion cracking of the highly stressed turbine materials.

Hydrazine thermally decomposes above ca. 200°C with the rate increasing with temperature. Consequently, residual hydrazine is not significantly present in the boiler water blowdown from high pressure, conventional boiler plant.

Optimising Hydrazine Use and Supply/Handling Considerations

The adverse operational consequences of the alternative reagents lead to the continued favouring of hydrazine as the primary oxygen scavenger reagent in this application. The focus for the industry has been on optimising its use to minimise any hazards:

- by minimising reagent use although details may vary depending on individual plant circumstances, plant operational guidance would be expected to include an indicative guideline on maintenance of a minimum amount of excess hydrazine in the process water systems – for example 2x residual dissolved oxygen level;
- by temporarily stopping using hydrazine whenever operationally possible normally during steady load operation with good mechanical deaerator performance. This is currently the favoured approach;
- by minimising handling of hydrazine hydrate solutions by the employees the reagent is delivered in polycans or Intermediate Bulk Containers with a preference for pre-diluted reagent where this is appropriate.

Sites using hydrazine will be equipped with appropriate plant and equipment, ensure appropriate maintenance of the equipment, will have developed and applied appropriately optimised procedures for material delivery, handling & usage and have suitably trained staff having regard for meeting applicable chemical use health and safety regulations. This may include regular checks of atmospheric conditions to confirm STEL (short-term exposure limits) is complied with and their subsequent recording.

6.1.3 Limiting Factors for the Uptake of Alternatives

The above discussion has already explained the key limiting factors for alternative substances which may vary by substance but can be summarised as follows:

- potential lack of or low passivating capabilities (e.g. sulphites, MEKO);
- potential impairment of oxygen scavenging performance at low temperatures (e.g. sulphites, carbohydrazide);
- low rates of oxygen removal and sluggish kinetics (e.g. DEHA);
- formation of organic acids (e.g. DEHA and other amines);
- release of CO₂ requiring additional neutralising amines to maintain pH at sufficiently high levels (e.g. carbohydrazide, amines);
- higher required dosage (applies across the board for the identified alternatives);
- release of hydrazine during use (e.g. carbohydrazide).

6.1.4 Requirements for Future Work on Alternatives

Alternatives are already available; there has been no specific proposition by consultees on what can be done for the current shortcomings to be overcome. Some discussion on alternative techniques and their prospects is provided in Confidential Annex 4.

6.2 Alternative Reducing Agents for Metals

6.2.1 Alternatives for Metal Deposition

6.2.1.1 Availability and Identities/Description of Alternatives

Alternative reducing agents that that been identified in literature as relevant to the electroless plating of nickel are shown in **Table 6.4**.

Table 6.4: Alternative Reducing Agents for Electroless Deposition of Nickel					
Name of alternative substance	Formula	EC Number	CAS Number		
Sodium hypophosphite (typically used in its hydrated form)	NaPO ₂ H ₂	231-669-9	7681-53-0		
Sodium borohydride	NaBH ₄	241-004-4	16940-66-2		
Dimethylamine borane (DMAB)	(CH ₃) ₂ NHBH ₃	200-823-7	74-94-2		
N-diethylamine borane (DEAB) $(C_2H_5)_2NHBH_3$ 2670-68-0					
Source: Jerry Barker Consultants (2010); Barnstead & Morcos (2009); Davis (2000)					

Hypophosphite-based baths: the basic chemical reaction for the deposition of nickel using hypophosphite as reducing agent is as follows (Electroplating Chemicals, 2010):

$$2 H_2 PO^{2-} + 2 H_2 O + Ni^{2+} \rightarrow Ni + H_2 + 2 HPO_3^{2-} + 4 H^+$$

Hydride ions may also react with hydrogen ions, thereby reducing the efficiency of hypophosphite utilisation. The electroless nickel deposits are not pure nickel but contain about 3-15% phosphorus, depending on bath composition and process conditions (Sidorenko & Kukin, 1977; Mittal, 1998; and Bicak *et al*, 2002).

The majority of electroless nickel used commercially is deposited from solutions reduced with sodium hypophosphite. The principal advantages of these solutions over these reduced with boron compounds or hydrazine include lower cost, greater ease of control and better corrosion resistance of the deposit. Early electroless nickel formulations were ammoniacal and operated at high pH. Later, acid solutions were found to have several advantages over alkaline solutions. Among these are: (a) higher plating rate, (b) better stability, (c) improved deposit corrosion resistance. Accordingly, most hypophosphite reduced electroless nickel solutions are operated between 4.5 and 5.5 pH, at 88-95°C. Their plating rate is approximately 25 μ m/h (Davis, 2000).

Borohydride-based baths: the reaction mechanism occurring with borohydrides has been quoted as follows (Electroplating Chemicals, 2010):

NaBH₄ + 4 NiCl₂ + 8 NaOH \rightarrow 4 Ni + NaBO₂ + 8 NaCl + 6 H₂O or 2 NaBH₄ + 4 NiCl₂ + 6 NaOH \rightarrow 2 Ni₂B + 8 NaCl + H₂ + 6 H₂O

These are only schematic representations since the details of the actual reactions are unknown. The borohydride anion is the most powerful reducing agent available for electroless nickel plating (any water-soluble borohydride can be used, although sodium borohydride is preferred) (Davis, 2000).

These reactions result in the deposition of an alloy containing 5-7% boron (Electroplating Chemicals, 2010). Borohydride baths are operated between 10 and 14 pH, at 25-95°C. Their plating rate is approximately 15-20 μ m/h (Davis, 2000).

Amine borane-based baths: the reaction mechanism occurring with amine boranes has been quoted as follows (Electroplating Chemicals, 2010):

Coatings containing between 1 and 5% boron are deposited.

Amine borane baths are operated between 5 and 7 pH, at 65-70°C. Their plating rate is approximately 7-12 μ m/h (Davis, 2000) and depends on the temperature and pH of the bath employed. This is lower than the plating rate in the much hotter borohydride baths, but quite adequate for the thin initial coatings required on plastics.

By way of comparison, the depositions produced from hydrazine solution contain 97-99.2% nickel. The rate of deposition is very dependent on pH, with virtually no deposition below 10.3, but with deposition rate over 12 μ m/hr at pH 11.0 (Electroplating Chemicals, 2010). Hydrazine baths operate at 90-95°C and, because of the instability of hydrazine at high temperatures, these baths tend to be unstable and difficult to control (Davis, 2000).

Literature does not provide readily available information on alternative reducing agents for the deposition of other metals.

6.2.1.2 Practical Experience of EU Stakeholders with Alternatives

Some information has been received from **Company 1** in relation to electroplating. Some hydrazine-free products (hydroxylammonium compounds and hydroxy acids) are available but it is claimed that there is some customer resistance to change. The company notes however, that it has not actually manufactured its relevant hydrazine-containing product for some time.

6.2.2 Alternatives for the Production of Precious Metals

6.2.2.1 Availability and Identities/Description of Alternatives

Alternative Substances

Gold refining: in the *aqua regia* process, alternative reducing agents to hydrazine include the substances shown in **Table 6.5**.

Table 6.5: Alternative Reducing Agents for Gold Refining in the Aqua Regia Process				
Name of alternative substance	Formula	EC Number	CAS Number	
Ferrous sulphate ("Copperas")	FeSO ₄	231-753-5	7720-78-7	
Sodium bisulphite	NaHSO ₃	231-548-0	7631-90-5	
Sulphur dioxide (gas)	SO ₂	231-195-2	7446-09-5	
Oxalic acid	HO(O)C-C(O)OH	205-634-3	144-62-7	
Hydroquinone	HO-C ₆ H ₄ -OH	204-617-8	123-31-9	
Certain sugars Various				
Source: Corti (2002)				

Precious metal precipitation from salt solutions: substances that have been identified as potentially relevant include:

- formic acid (HCOOH, EC Number: 200-579-1, CAS Number: 64-18-6) and formiates. **Company 42** is aware of testing that has been undertaken to establish whether these are suitable as reducing agents for the production of precious metals;
- sodium borohydride (NaBH₄, EC Number: 241-004-4, CAS Number: 16940-66-2). Company 31 and Frankham & Kauppinen (2010) describe this as an alternative in relation to PGMs; and
- thioform ((CH₂S)₃, EC Number: 206-029-7, CAS Number: 291-21-4) and zinc. Phillips (2005) suggests that thioform and zinc can be used to replace hydrazine in the removal of PGMs from effluents, but these also carry their own problems and can make effluent disposal costly.

Recovery of gold through active carbon elution: McDougall & Hancock (1981) identify hydroquinone as a suitable reducing agent for the recovery of gold through active carbon elution methods (Actired® appears to fall under this category).

Alternative Techniques

Phillips (2005) reports that for a safe and more environmentally friendly recovery of platinum group metals (PGMs), Smopex® fibrous precious metal scavengers can be used. These can recover PGMs from process or effluent streams. The fibres consist of a polypropylene or viscose backbone (making them suitable for use in both organic and aqueous streams), grafted with specific functional groups that can selectively remove PGMs from solution⁴⁰.

Smopex® is capable of recovering PGMs down to ppb levels and with metal loadings in the region of 10% wt (that is 100 g metal/kg fibre) the quantity of fibre required to achieve satisfactory recovery is not large. The fibres are thermally stable up to at least 120°C so they can be used at elevated temperatures, where metal recovery is often easier (Phillips, 2005).

Smopex® fibres are non-hazardous and, after washing with water can be returned for refining of the captured metal (Phillips, 2005). Preliminary input from a company with experience in these methods would appear to suggest that Smopex® tends to be used for the removal of precious metals from very dilute solutions only as it has a fixed number of active sites to which precious metals may bind. Smopex® is a relatively non-specific scavenger of precious, base and heavy metals from their dilute solutions and is not a reducing agent, so it does not directly compare to hydrazine. Some additional information is provided in Confidential Annex 4.

6.2.2.2 Practical Experience of EU Stakeholders with Alternatives

Company 42: this is a company precipitating precious metals (PGMs) from solutions. The company notes that depending on temperature, pH-value and speed of the addition, hydrazine is a well-controllable reducing agent and leads to good results with regard to the selectivity and efficiency of the reaction. Formic acid and formiates are very hard to control in comparison to hydrazine and have resulted in the past in serious accidents, caused by spillage of hot reaction solution. The company also notes that potential substituents have to fulfil the condition that they and their reaction products do not contaminate the PGMs formed in the refining process. The purity of the metals has to reach a minimum of 99.95%. Apparently, this cannot be achieved with formiates.

Company 31: this company uses a very small volume of hydrazine hydrate solution for the precipitation of metals from scrap and indicates that it would be able to switch to sodium borohydride. The latter has already been successfully tested in laboratory conditions.

Some additional information on the availability and suitability (or lack thereof) of alternatives to hydrazine in the precipitation of precious metals is provided in Confidential Annex 4.

6.2.3 Alternatives for the Production of Basic Metals

Some information is available in Confidential Annex 4.

⁴⁰ More information on Smopex is available here: <u>http://www.smopex.com/site.asp?id=1190&pageid=1205</u>

6.3 Alternatives for Effluent Treatment

6.3.1.1 Alternative Substances

Some information is available in literature on the availability of reducing agents for the noncatalytic removal of NO_x gases from waste streams. Lyne (2002) suggests that reducing agents, apart from hydrazine, include the substances shown in **Table 6.6**.

Table 6.6: Alternative Reducing Agents for Effluent Treatment					
Name of alternative substance	Formula	EC Number	CAS Number		
Hydroxylamine	NH ₂ OH	232-259-2	7803-49-8		
Hydroxylamine sulphate	$(HONH_2)_2.H_2SO_4$	233-118-8	10039-54-0		
Sulphamic acid	H ₂ N.SO ₃ H	226-218-8	5329-14-6		
Urea H ₂ N-CO-NH ₂ 200-315-5 57-13-6					
Source: Lyne (2002)					

These reagents all have in common the amine group $(-NH_2)$, and theoretically react to reduce NO_x dissolved acid by a reaction such as:

4 HNOSO₄ + 3 N₂H₄
$$\rightarrow$$
 5 N₂ + 4 H₂SO₄ + 4 H₂O

In practice, only hydrazine and to some extent hydroxylamine are effective at the conditions of temperature and residence time typically available in an acid plant. Pure sulphamic acid or urea will reduce the NO_x only in weaker acid solutions, and by-product $(NH_4)_2SO_4$ may contaminate the treated product. The reducing agent must be added in excess to achieve adequate destruction of NO_x, and post treatment with H₂O₂ to destroy the excess reductant is then required. However, hydroxylamine or hydroxylamine sulphate are less toxic and easier to handle than hydrazine (Lyne, 2002).

6.3.1.2 Consultation Findings

No information specific to this use was made available from consultees.

6.4 Alternative Aerospace Propellants

6.4.1 Availability and Identities/Description of Alternatives

6.4.1.1 Recent EU Research on 'Green' Propellants

The high vapour toxicity and large vapour pressure of hydrazine, coupled with the desire to both improve operational response and significantly increase performance, present significant technical challenges to be overcome in producing next-generation monopropellants. Low toxicity or 'green' propellants have been studied by several organisations around the world.

The propellants fall into three groups, those intended for launchers and upper stages, replacement of existing propellants used on orbital transfer vehicles, and those intended to replace current storable bi- and monopropellants used on spacecraft (Caramelli, 2008).

Of most relevance to hydrazine (and its main use as a monopropellant in spacecraft) is Caramelli's 2008 overview of recent and on-going EU R&D in the field of spacecraft propellants and propulsion. As shown in **Table 6.7**, R&D activities in European industry, research institutes and organisations related to 'green' propellants were concentrated in Sweden in 2008 and this still appears to be the case. Substantial R&D activities in these technologies were also performed in Italy and Austria. Limited R&D activities were also reported in France, Germany, Netherlands and UK.

Organisation	Name of Item	Remarks		
SSTL (UK)	 Catalyst investigations Hydrogen peroxide and nitrous oxide propulsion developments 'Green' propulsion systems flown on small satellites Micro-electro-mechanical systems (MEMs) 	 N₂O resistojet 125 mN thrust Bipropellant – hydrogen peroxide / Kerosene engine up to 40N TRL 6 N₂O, butane, water propulsion systems flown on small satellites, including ESA Giove-A (Galileo) MEMs High Test Peroxide (HTP, H₂O₂) engine concluded ESA contract 		
University of Surrey/SSTL (UK)	 Hydrogen peroxide and nitrous oxide propulsion developments N₂O 	 H₂O₂ hybrid engine development: 'Pancake' configuration H₂O₂ long term storage tank technologies N₂O catalytic decomposition with CNES and Russian Scientific Centre for Applied Chemistry, INTAS contract 		
University of Southampton (UK)	Hydrogen peroxide catalysis	• H ₂ O ₂ homogeneous catalyst investigations (with DELTACAT (UK))		
ECAPS (SE)	Development of ADN based propulsion systems, space qualification of HPGP (High Performance 'Green' Propellant) propulsion systems, including: - 1 N engine Propellant LMP-103S	 Ground qualified 1N thruster with ADN LMP-103S Manufactured a propulsion S/S with 1N ADN thruster to fly with PRISMA S/C 5 N and 22 N are in development-performed 22N engine hot firing tests based on ADN propellant and investigating continuous scale-up for launcher applications Developed and tested LMP-103S propellant 		
FOI (SE)	 Development of advanced liquid monopropellants based on ADN 'Green' solid propellants 	Production and hazard testing of LMP-103S ADN-based propellant FLP-106 development, hazard testing, compatibility, stability and characterisation New ADN-based propellant with higher I_{sp} (~260s) and density and with lower vapour pressure, related high temperature resistant materials and components need development Investigation of ADN as an oxidiser for solid propellants		
Austrian Research Centers (AT)	Hydrogen peroxide monopropellant and bipropellant thrusters	 Development of a 0.5 - 1.5 N H₂O₂ monopropellant thruster (I_{sp} =160 s) utilising advanced monolithic catalyst (LACCO) Development of a bipropellant thruster utilising H₂O₂ and Kerosene, I_m =280-330 s 		

Table 6.7: Expertise and Research on 'Green' Propellants for Spacecraft within Europe (2008)				
Organisation	Name of Item	Remarks		
LACCO (FR)	Catalyst investigations	• Investigations with a batch reactor on various propellants		
EDOTEK (UK)	DMAZ (2- dimethylaminoethylazide) – a liquid fuel)	Reactivity investigations		
University of Naples (IT)	Catalyst investigations, hybrid propulsion	 Hydrogen peroxide investigations (decomposition of hydrogen peroxide with advanced catalysts) 		
ALTA (IT)	 Hydrogen peroxide thrusters Collaboration with Southampton University (UK) 	 Development of 5N to 10N and 25N monopropellant H₂O₂ thrusters for future bipropellant peroxide-ethane thruster prototype Optimisation of advanced catalytic beds for HTP decomposition Throttleable H₂O₂ bipropellant technologies with National funding contract Self-pressurised 'green' propellant technology Development of 50 N bipropellant peroxide-ethane thruster prototype (TRL 4-5, performance target 200-500 N) in collaboration with University of Southampton 		
AI: Aerospace Innovation (DE)	Electro-thermal propulsion	 Water and gas resistojet systems for small satellites under development To be flown on TET-1 satellite 		
DELTACAT Ltd (UK)	Hydrogen peroxide thrusters	• In conjunction with ALTA and the University of Southampton		
TAS (IT)	Hybrid systems in cooperation with University of Padova (CISAS)			
Source: Caramelli	i (2008)	•		

Notably, the focus of research on alternative, 'greener' propellants is so far on finding substitutes for monopropellant hydrazine. Limited work is currently undertaken in relation to substitutes for MMH; some work is on-going in the FP7 project GReen Advanced Space Propulsion (GRASP), funded by the EC^{41} (Swedish Defence Research Agency, 2010).

6.4.1.2 Recent Research outside the EU

According to Caramelli (2008), little is known about potential developments in the USA for spacecraft 'green' propellants. Work is still continuing in universities on hydrogen peroxide, in the USA as well as in Japan. Hybrid propulsion is being pursued in the US, the most high profile example being SpaceDev who manufacture the hybrid engine for Space Ship One. As will be discussed later in this Section, some work is currently undertaken in the USA on the development of a propellant based on hydroxylammonium nitrate (HAN).

⁴¹ Details available here: <u>http://www.grasp-fp7.eu</u>.
6.4.1.3 Availability and Identities/Description of Alternative Monopropellants

Overview

Two major efforts have developed over the last 15-years and have focused on advanced monopropellant compositions produced from energetic ionic compounds – one coming from Europe (Sweden) and the other coming from the USA (the US Air Force). While the European monopropellant is based on ammonium dinitramide (ADN, NH₄N(NO₂)₂, CAS Number: 140456-78-6), the US Air Force Research Laboratory's (AFRL) effort focuses on hydroxylammonium nitrate (HAN, NH₃OH.NO₃, EC Number: 236-691-2, CAS Number: 13465-08-2). While a significant amount of literature exists on the characteristics of the European monopropellant, very little literature is available regarding AF-M315E, the codename for the HAN-based monopropellant currently developed in the USA (Hawkins *et al*, 2010).

Other possible alternatives includes propellants based on hydrogen peroxide (H_2O_2 , EC Number: 231-765-0, CAS Number: 7722-84-1), which is apparently a somewhat older technology. Hydrazinium nitroformate (HNF, $N_2H_5C(NO_2)_3$, CAS Number: 20773-28-8) has also been mentioned as a monopropellant that has been looked at in the past (Schmidt & Wucherer, 2004).

On the other hand, hydrazine derivatives such as MMH and UDMH are widely used as bipropellants.

Alternatives based on Ammonium Dinitramide

ADN is a promising oxidiser in propellants due to its high solubility. A number of different ADN-based liquid monopropellants have been developed during the last years. Among them, the formulations FLP-106 and LMP-103S have received particular attention. LMP-103S has been selected by the Swedish Space Corporation (SSC)/ECAPS and FLP-106 has been selected by the Swedish Defence Research Agency (FOI) as main monopropellant candidates for further development efforts (Wingborg & de Flon, 2010).

The Swedish company that markets the LMP-103S propellant suggests that the product is low toxic, environmentally benign and provides increased performance compared with hydrazine. Its specific impulse (I_{sp}) is 6% higher and propellant density is 24% higher, resulting in a 30% increase in density-specific impulse. Its composition is 3-6% ammonia, 15-20% methanol and 60-65% ADN, balanced with water; the exact composition is not public information (ECAPS, undated).

With regard to the comparison of toxicity of ADN to that of hydrazine (and to that of pure HAN), Eurenco (2004) provides some information which is reproduced in **Table 6.8**.

Propellant	LD ₅₀ rat, oral (mg/kg)
ADN/glycerol/water	1,360
HAN (pure)	325
Hydrazine	59

Company 25 argues that LMP-103S is suitable as a propellant for space propulsion, space transportation, specific propulsion systems and gas generators. The company has been working on the development of LMP-103S for more than ten years.

LMP-103S is claimed to be long-term compatible with most construction materials used in hydrazine commercial-off-the-shelf (COTS) components and propulsion systems. It is transport classified according to UN Class 1.4S (using a specific transport container), allowing air transportation in passenger and cargo carriers. SCAPE-suits⁴² are not required when handling the product; what is required is regular chemical protective clothing (rubber gloves, eye and respiratory protection). LMP-103S is long-term storable and, unlike hydrazine, not sensitive to contact with air and humidity (ECAPS, undated).

With regard to the other ADN-based formulation, FLP-106, this is a low viscous yellowish liquid with high performance, low vapour pressure and low sensitivity. It is based on a low volatile fuel, water and 64.6% ADN (Wingborg & de Flon, 2010).

Compatibility assessment using a heat flow calorimeter was performed with several materials used in propulsion systems. The results show that FLP-106 is compatible with stainless steels, alloys based on nickel-chromium and titanium and polymers such as PTFE (polytetrafluoroethylene) and Kalrez⁴³. The polymers EPDM (ethylene propylene diene monomer rubber) and PETG (polyethylene terephthalate glycol copolymer) had a slight shift in colour but still seem, based on the heat flow measurements, to be compatible with FLP-106 (Wingborg & de Flon, 2010)⁴⁴.

From the shock sensitivity testing it was concluded that FLP-106 should be considered as a hazard class 1.1 material (Wingborg & de Flon, 2010).

FLP-106 has a similar oral toxicity and should be considered as harmful, but not toxic. However, FLP-106 has a substantially lower vapour pressure than LMP-103S and requires no respiratory protection during handling. The advantage using FLP-106, apart from its lower volatility, is its higher performance and higher density as shown in **Table 6.9** (Wingborg & de Flon, 2010).

Propellant	FLP-106	LMP-103S	
Specific impulse, $I_{sp}(s)^*$	259	252	
Density, ρ (g/cm ³) **	1,357	1,240	
$2 \cdot I_{sp} (gs/cm^3)$	351	312	

⁴² Self-contained Atmospheric Protective Ensemble.

⁴³ A perfluoroelastomer supplied by DuPont.

⁴⁴ Hydrazine, on the other hand, is compatible with stainless steels (303, 304, 321 or 347), nickel and 1100 and 3003 series of aluminium. Iron, copper and its alloys (such as brass or bronze), monel (Ni/Cu alloys), magnesium, zinc and some types of aluminium alloy must be avoided (Sutton & Biblarz, 2010).

** at 20°C

Alternatives based on Hydroxylammonium Nitrate

AFRL's approach to replacing hydrazine is the synthesis and development of energetic compounds/formulations with substantially less vapour toxicity and superior performance (specific impulse and density). In the past, such efforts often attempted to produce low melting point salt mixtures containing toxic hydrazines and amines as melt point depressants (Hawkins et al, 2010). HAN is suited as an oxidiser in ionic monopropellants because it is highly soluble in water – at room temperature, up to 96% HAN can be dissolved in water. A team at Olin Aerospace (now Aerojet-Redmond) in the USA recognised this potential and began testing HAN-based monopropellants in a catalytic rocket engine reactor in 1992. Various water soluble fuels have been tested over the years, including (in chronological order) triethanolammonium diethylhydroxyl-ammonium nitrate, glycine, glycine nitrate. nitrate, methanol, hydroxyethylhydrazinium nitrate, tris(2-aminoethyl) ammonium trinitrate and others. Various catalysts have been tested (Schmidt & Wucherer, 2004).

The key monopropellant based on HAN is called AF-M315E. Testing results for AF-M315E indicate that a >50% improvement in propulsion system performance over hydrazine is achievable while simultaneously providing a safer environment for the general public, ground personnel, crews and flight participants (Hawkins *et al*, 2010).

Hazard testing of HAN-based propellants has indicated that they are class 1.3 explosive materials – comparable to many of the common solid propellants used in boosters and missiles. This represents a different level of hazard vs. the non-explosive monopropellants hydrazine and 90% hydrogen peroxide (Schmidt & Wucherer, 2004).

Hawkins et al (2010) discuss some key toxicological parameters of the AF-M315E propellant:

- **acute oral toxicity**: the acute oral LD₅₀ of AF-M315E was estimated to be 550 mg/kg in the female rat with a 95% PL confidence interval of 385.3 to 1,530 (also note the LD₅₀ value for rodents given for 'pure' HAN in **Table 6.8**). Since the oral LD₅₀ of hydrazine is ca. 60 mg/kg in the rat, AF-M315E is reported as being an order of magnitude less toxic by the acute oral route;
- acute skin irritation: an acute skin irritation study of AF-M315E was pursued through administration by the dermal route to rabbits. Exposure to the propellant produced very slight erythema at ¹/₃ of the test sites by the 1-hour scoring interval. Complete resolution of the dermal irritation occurred by 72 hours post-dose. Under the conditions of the test, AF-M315E was considered to be a slight irritant to the skin of the rabbit based on the EPA FIFRA⁴⁵ Dermal Irritation Descriptive Classification. According to the EEC Dermal Evaluation Criteria, AF-M315E was considered to be a non-irritant for erythema and oedema. In comparison, hydrazine is considered such a strong irritant that it is labelled as corrosive, according to Hawkins *et al* (2010);
- **dermal sensitisation**: a sensitisation study was undertaken for AF-M315E administered by the dermal route using the Modified Buehler Design. The dermal sensitisation potential of AF-M315E was evaluated in Hartley-derived albino guinea pigs. Based on the results of this study, AF-M315E is not considered a contact sensitiser in guinea pigs. Hydrazine by comparison is a strong allergen or potent sensitising agent; and

⁴⁵ US Federal Insecticide, Fungicide, and Rodenticide Act

• Ames test for mutagenicity: an Ames evaluation of AF-M315E for mutagenic activity was conducted using *Salmonella-Escherichia coli* microsome plate incorporation assay. AF-M315E was judged mutagenic under some test conditions used in this study; therefore, the test substance was determined to be positive in the bacterial reverse mutation assay. Although AF-M315E is identified as mutagenic, it appears to be a weak mutagen⁴⁶.

The overall toxicological profile of AF-M315E is such that the handling of the propellant does not require the self-contained breathing apparatus that is required when handling hydrazine. Instead, typical personal protective equipment (i.e., gloves, eye protection, and overalls/coats) is required (Hawkins *et al*, 2010).

Alternatives based on Hydrogen Peroxide

Review of past and current research: the earliest research on hydrogen peroxide-based rockets was conducted in Germany during the 1930s. Early engines based on using a catalytic bed to generate a hot stream of oxygen and steam were used in the ME163 fighter plane and to drive the V2 turbine pump. Since the 1990s, there has been a renewed interest in hydrogen peroxide engines, generated mainly by the need for less toxic propellants. However, with the exception of a very few research engines, this has not yet led to any new flight hardware (Cervone *et al*, 2006).

As a direct consequence of the renewed interest in the use of hydrogen peroxide shown by the rocket propulsion community, Alta S.p.A. (Italy) and DELTACAT Ltd. (UK) were recently carrying out a joint activity for the development of hydrogen peroxide monopropellant thrusters based on the use of advanced catalytic beds (see **Table 6.7**). This activity was funded by the European Space Agency and its objective was the design and realisation of two prototype thrusters (a 5 N and a 25 N one), in which catalytic beds made of different catalyst materials and substrates will be installed and assessed (Cervone *et al*, 2006).

Hydrogen peroxide action as a propellant: hydrogen peroxide is a high density liquid having the characteristic of being able to decompose exothermically into water (steam) and oxygen according to the reaction (Cervone *et al*, 2006):

$$H_2O_2 (l) \rightarrow H_2O (g) + \frac{1}{2}O_2 (g)$$

The physical properties of hydrogen peroxide are close to those of water, with two notable differences: H_2O_2 has a significantly higher density and a much lower vapour pressure. It remains in the liquid state at ambient pressure in a wide range of temperatures and is relatively easy to handle with respect to other common liquid rocket propellant oxidisers like dinitrogen tetroxide, nitric acid and liquid oxygen (Cervone *et al*, 2006).

The propulsive performance of hydrogen peroxide monopropellant rockets is about 20% lower than hydrazine, but the volume specific impulse achievable with 90% H_2O_2 is higher than most other propellants due to its high density. This is particularly useful for systems with significant aerodynamic drag losses and/or stringent volume constraints. With respect to bipropellant and

⁴⁶ Hawkins *et al* (2010) emphasise that it is "*exceedingly difficult*" to develop an advanced propellant that will not possess some mutagenic potential because of the chemical structures involved for energetic materials. Advanced energetic propellant compositions that have been championed for environmentally enhanced or 'green' propulsion have included mutagens – examples include hydrazinium nitroformate (HNF) or ADN. Also of note is that there is not EU classification for mutagenicity for hydrazine under the CLP Regulation No 1272/2008 but some GHS classifications refer to it as a suspected mutagen.

hybrid rocket engines, hydrogen peroxide yields a specific impulse comparable to other liquid oxidisers like dinitrogen tetroxide, nitric acid and even liquid oxygen (Cervone A *et al*, 2006).

A Swedish company was until recently selling propellant grade H_2O_2 with a purity of 80-90%. The propellant required a decomposition catalyst such as a silver catalyst or a ceramic catalyst with platinum coating to decompose it into water and oxygen (Peroxide Propulsion, 2010). The Swedish company suffered a devastating accident earlier in 2010 and has since ceased the production of H_2O_2 propellants⁴⁷.

Wernimon *et al* (2009) refers to different space missions where H_2O_2 81-91% was used. This source suggests that the H_2O_2 propellants may be preferred where the avoidance of the toxic effects of hydrazine is important, and for missions where the exhaust products from hydrazine decomposition (ammonia, hydrogen and nitrogen) may also be undesirable. In general, the missions where substitution of hydrogen peroxide for hydrazine would be beneficial are those with repetitive human interaction or repetitive environmental interaction. Caramelli (2008) notes that, in the case of H_2O_2 , it is critical that long-term storage of the propellant is addressed before this propellant could be considered for a medium to long-term mission.

Alternatives based on Hydrazinium Nitroformate

HNF was identified as a promising ingredient for new, high performance solid propellant in 1989 in a desk study that was awarded to TNO by European Space Agency to review the future options for increase of performance of space propulsion in general (Ciucci *et al*, 2004).

The substance forms yellow crystals with a melting point of 124° C and a UN transport classification of 1.1 D (APP, 2010). HNF solid crystals can be dissolved in water to produce a HNF-based monopropellant (but it is suggested that a more cost-effective and safe method would be to directly produce the monopropellant without crystallisation) (Marée *et al*, 2004). Back in 2002, Schoyer *et al* suggested that liquid HNF monopropellants look attractive as a hydrazine replacement. They offer the same or a substantially higher specific impulse, combined with a 30-40% higher density.

A Dutch-based company claims to be the sole commercial producer of HNF world-wide (APP, 2010). It should be noted that its main intended use is as a solid propellant.

Marée *et al* (2004) have compared two HNF-based propellant formulations (codenamed APPML 21 and APPML 22) to hydrazine. A comparison of toxicity of HNF-based blends to hydrazine and hydrogen peroxide was provided and is reproduced here as **Table 6.10**.

Table 6.10: Comparison of Toxicity Data of HNF Blends to Hydrazine and Hydrogen Peroxide Propellants							
Parameter	Propellant						
	APPML 21	APPML 22	Hydrazine	$H_2O_2(90\%)$			
LC ₅₀ inhalation (ppm)	>>900 - 40,000	>>900 - 40,000	570	1,680			
LD ₅₀ dermal (mg/kg)	4,000	3,600	93	4,060			
LD ₅₀ oral (mg/kg)	256	232	60	376			

⁴⁷ A relevant news item on the incident is available here: http://www.hobbyspace.com/nucleus/index.php?catid=45&blogid=1&archive=2010-07

ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

Vapour pressure (mbar)	0.5	0.5	14	2		
Source: Marée et al (2004)						

Inhalation toxicity: the data shown by Marée *et al* suggest no indication of danger with respect to inhalation. Some uncertainty exists on the exact value of LC_{50} for APPML 21 and 22 due to the fact that, in experiments with one of the propellant constitutents, no vapour concentration with lethal effects could be reached. One reference could be found which would result in a LC_{50} of 40,000 ppm. In addition, the vapour pressures for HNF propellants in comparison to hydrazine and hydrogen peroxide are low; this combined with a high LC_{50} value would reduce the inhalation hazard. However, this salt is a highly energetic material. To prevent the risk of introducing other hazards during handling, it would be advantageous if the evaporation of the water/solvent and fuel could be prevented or significantly slowed down (Marée *et al*, 2004).

Skin toxicity: the propellants may be harmful to the skin, hence the correct clothing should be used. The LD_{50} value for the dermal route would still have to be verified experimentally. If swallowed, APPML 21 and 22 would be toxic, but still the LD_{50} values are more favourable than hydrazine and comparable to hydrogen peroxide (Marée *et al*, 2004).

Oral toxicity: this is lower than hydrazine. The risk of swallowing the propellant during handling is far lower than inhalation or dermal contact (Marée *et al*, 2004).

Long-term toxicity: the long-term toxicity effects still had to be evaluated. However, based on the constituents, a Maximum Allowable Concentration value of 50 ppm was expected in comparison to 0.1 ppm for hydrazine and 1 ppm for hydrogen peroxide (Marée *et al*, 2004).

In summary, the foreseen fuels discussed by Marée *et al* (2004) are relatively volatile and slightly toxic. More research was reportedly required on physical compatibility, sensitivity, stability and storage life aspects. Furthermore, catalytic ignitability would be investigated at laboratory and batch reactor scale. Direct production methods reducing production cost and increasing process safety would be examined (Marée *et al*, 2004).

Hydrazine Derivatives as Propellants

Monomethyl hydrazine (MMH, CH₃NHNH₂, EC Number: 200-471-4, CAS Number: 60-34-4) and unsymmetrical dimethylhydrazine (1,1-dimethylhydrazine, UDMH, (CH₃)₂NNH₂, EC Number: 200-316-0, CAS Number: 57-14-7) may be used in bipropellants. The hazardous properties of these derivatives are discussed and compared to those of hydrazine in Section 1.1.1.

Monomethyl hydrazine: MMH is miscible with water, hydrazine, hydrazine derivatives, amines and lower weight monohydric alcohols. MMH is a mildly alkaline base and a very strong reducing agent (Arch, 2010b).

The major use of MMH is in the aerospace industry. It is used as a propellant and for spacecraft orbital control thrusters. MMH may also be used in chemical synthesis where both an N-N bond and a methyl group are desired (for instance, in pesticides (K&Y, 2010)). Many patents have been issued covering applications of MMH in petroleum refining, explosives, metal treating, photography, fibres, coatings and resins (Arch, 2010e).

MMH is preferred over hydrazine for use in bipropellants. One reason for this might be its lower freezing point. MMH is also more thermally stable and can be used as a coolant in regenerative cooled rocket engines (Swedish Defence Research Agency, 2010).

MMH has a better shock resistance to blast waves and a better liquid temperature range than high purity hydrazine. Like hydrazine, MMH vapours are easily ignited in air and the materials compatible with hydrazine are also compatible with MMH. The specific impulse with storable oxidisers is typically 1-2% lower with MMH as opposed to hydrazine (Sutton & Biblarz, 2010).

MMH may be added in small quantities (3-15%) to hydrazine to give a substantial quenching effect on the explosive decomposition of the latter (Sutton & Biblarz, 2010).

Unsymmetrical dimethylhydrazine: UDMH is miscible with water, hydrazine, dimethylhydrazine, ethanol, amines and most petroleum fuels. UDMH is mildly alkaline and is a very strong reducing agent (Arch, 2010c).

The major use of UDMH is in the aerospace industry, where it is primarily used as a propellant. It is also used in chemical synthesis, where an N-N bond and two methyl groups are needed (e.g. in the synthesis of photographic chemicals). It has also been used in acidic gas absorbers and as a fuel stabiliser (Arch, 2010e). A Chinese source further suggests uses in the plastics, rubbers and dyestuff industries (K&Y, 2010).

UDMH may be used instead of or in mixtures with hydrazine as it forms a more stable liquid, particularly at higher temperatures. Furthermore, it has a lower freezing point (-57.1°C) and a lower boiling point (63.5°C) than hydrazine. When UDMH is burnt with an oxidiser, it gives slightly lower values of specific impulse than high purity hydrazine. UDMH is often used when mixed with 30-50% anhydrous hydrazine (Aerozine is a 50:50 mixture) or with 25% hydrazine hydrate (this is UH 25, a fuel mixture for rockets; it was developed for the European Ariane 2-4 launch vehicles). UDMH is typically used in Russian and Chinese rocket engines and small thrusters (Sutton & Biblarz, 2010), but will also be used in the newly developed European launcher VEGA⁴⁸ (Swedish Defence Research Agency, 2010).

6.4.2 Practical Experience of EU Stakeholders with Alternatives

6.4.2.1 Alternatives based on Ammonium Dinitramide

The 1 N class rocket motor based on LMP-103S is qualified for the PRISMA mission and is now being demonstrated in-space. The PRISMA project was established in early 2005, when the Swedish Space Corporation formulated a mission concept consisting of two satellites and a series of experiments in order to test formation flying and rendezvous technology in a real space mission (PRISMA Satellites, 2010).

The two PRISMA satellites were launched in June 2010 on a year-long mission to test several new technologies alongside the principal mission of performing formation-flying manoeuvres between the two spacecraft. A key mission goal is to demonstrate high autonomy for the

⁴⁸ Its Fourth Stage AVUM (Attitude and Vernier Module) will have a propellant (UDMH/N₂O₄) mass of 550 kg, based on two clusters of three thrusters, each having a 50 N thrust. The first launch is planned for 2011 from Europe's Spaceport in French Guiana where the Ariane 1 launch facilities are being adapted for its use (see here: http://www.esa.int/SPECIALS/Launchers_Access_to_Space/ASEKMU0TCNC_0.html).

'active' satellite as it operates around the other, smaller satellite, which is in passive mode (de Selding, 2010).

Company 25 argues that the required performance, characteristics and life have been met and demonstrated on ground and in space on the PRISMA satellites. It goes on to suggest that LMP-103S can completely replace anhydrous hydrazine as a monopropellant and no additional R&D work is required. Some product re-design will be required, namely product design of thrusters for higher thrust levels. A further three years may be required for rocket motors already in development while five years may be required for the development of new rocket motors.

Reportedly, the company marketing the propellant hopes that, once the PRISMA results are known, this High Performance Green Propulsion (HPGP) system will find a commercial market. The company behind LMP-103S has advised that there are orders for the propellant by three satellite manufacture contractors.

The European Space Agency is reported to have confirmed that ADN has a 30% better performance than hydrazine, and is much less toxic. Reports available online corroborate the view that, unlike hydrazine, it is safe to transport by aircraft and can be worked with in "*shirt sleeves*" rather than protective suits. No energetic rocket fuel is ever going to be as benign as water, and the Agency does not expect to replace hydrazine completely but hopes to eventually provide industry with an acceptable alternative. Reducing the risk will lead to cheaper handling and a lower price tag on missions. The ultimate aim is to enable the shipping of satellites from their factory with full fuel tanks – right now they are fuelled at their launch site at the very last moment, for safety reasons (Messier, 2010).

Nevertheless, it should be remembered that existing programmes such as the Galileo depend on the use of hydrazine propellants. Therefore, the Agency does not believe that hydrazine can currently be replaced by alternatives. Indeed, the Agency delivered to RPA a letter stating its position in relation to the continued use of anhydrous hydrazine in aerospace applications. The letter, dated 9 December 2010 and signed by the Director of Technical and Quality Management and the Director of Launchers, states the following (European Space Agency, 2010):

"In addition to the survey on hydrazine submitted by industry, the European Space Agency (ESA) wants to emphasise in this letter the strategic importance of the use of hydrazine in propulsion systems for launcher and satellite programs. It is a fundamental component for the European space programs to assure access to space as well as to accomplish its space missions. Hydrazine propulsion technology is based on 50-60 years experience, and no alternative is available in long-term. A secured supply of hydrazine is vital for the current and future success of the European space program."

A similar position is taken by the Centre National d'Etudes Spatiales (CNES), the government agency responsible for shaping and implementing France's space policy in Europe, as well by key companies in the sector. For instance, **Company 15** has stated the following (edited excerpt):

"Today one considers that we have to secure the long term supply of a quality of hydrazine suitable for the spaces activities to maintain the strong position of the European Space Business. Our company (...) is involved in this project. Main characteristics for this use of anhydrous hydrazine are:

- the volume used for the space activities is very low (only several tons a year);
- a substitute to hydrazine is not yet identified. When (this) will occur, its qualification for space uses will require long (about 10 years) and very expensive work (millions of Euros);
- companies belonging to this supply chain are 'high tech' companies familiar with standards applicable to space operations, they are all aware of the classification from the CLP regulation and they keep on improving their processes to protect their employees and to preserve the environment.

It is therefore of the utmost importance to maintain a robust and strong position of the European community (space agencies and companies) in space activities to assure the autonomous European access to space."

6.4.2.2 Alternatives based on HAN, Hydrogen and HNF

There appears to be no experience with HAN-based monopropellants in the EU and no specific information has been retrieved on actual missions where these alternatives have been tested as hydrazine substitutes.

6.4.3 Limiting Factors for the Uptake of Alternatives

Some key issues that need to be addressed when it comes to the replacement of hydrazine propellants with alternatives include:

- the long-term storage of alternative propellants;
- materials compatibility metallic and non-metallic components currently qualified for use with hydrazine may not be automatically usable for a non-toxic alternative propellant (Schmidt & Wucherer, 2004). However, the proponents of the two ADN-based propellants mentioned earlier (FLP-106 and LMP-103S) claim that their products have acceptable compatibility with many of the relevant materials; and
- ignition for ADN-based monopropellants, the major challenge is ignition and more work is still needed in this area (Swedish Defence Research Agency, 2010). Hydrazine thrusters use catalytic ignition, which is simple and reliable. To replace hydrazine, an ADN-based monopropellant must be as easy to ignite. The high combustion chamber temperature is a matter of concern since it might deteriorate a catalyst bed. Catalytic decomposition of ADN has been studied by Amariei *et al* (2005). The results showed that the catalyst used had a weak influence on the ADN decomposition temperature. In fact, it was found that, in the presence of glycerol, the catalyst shifted the decomposition temperature to a higher value. Electrical ignition of ADN-based monopropellants has also been studied (Wingborg *et al*, 2006).

With particular regard to hydrogen peroxide, the most significant technology challenge for the realisation of hydrogen peroxide monopropellant thrusters is the development of effective, reliable, long-lived catalytic beds, giving fast and repeatable performance, insensitivity to poisoning by the stabilisers and impurities contained in the propellant, capable of sustaining the large number of thermal cycles imposed by typical mission profiles and not requiring (if possible) pre-heating for efficient operation. Currently, the most frequently used catalyst materials for H_2O_2 are metallic silver, permanganates of alkali metals, manganese oxides like manganese dioxide (MnO₂) and dimanganese trioxide (Mn₂O₃) (Cervone *et al*, 2006).

6.5 Alternatives for Submarine Rescue Systems

6.5.1 Availability and Identities/Description of Alternatives

There are two different propellants utilised for the gas generator of the submarine RESUS system: one containing hydrazine (a system including pressurant and catalyst bed) and another with a solid rocket propellant. The solid propellant gas generators produce pressurant gas by combustion (Astrium, 2010).

Table 6.11: Composition of Gas Generator Propellants for the Submarine RESUS System				
Characteristic	Liquid propellant	Solid propellant		
Propellant	Hydrazine	Glycidyl-Acido-Polymer (GAP) + Strontium Nitrate		
Propellant mass	62 kg	157 kg		
Outlet temperature	775 K	1075 K		
Gas composition	$\begin{array}{c} H_2 (46\%) \\ N_2 (28\%) \\ NH_3 (20\%) \\ H_2 O (6\%) \end{array}$	H ₂ (34%) CO ₂ (36%) H ₂ O (30%)		
Quantity required*	ca. 10	ca. 7		
Source: Astrium (2010c)				
* The number of gas generator	rs required is based on 80 m ³ MBT,	, 350 m depth and 100% blow out		

 Table 6.11 summarises the key differences between the two types of gas generators.

The hydrazine utilised in the gas generator is diluted with 6% or 8% water (Wernimon *et al*, 2009). The total solid propellant gas generator mass is almost double than for the hydrazine system and hence hydrazine is probably preferred for its smaller packaging and the lower exhaust gas temperatures (Wernimon *et al*, 2009).

Wernimon *et al* (2009) suggest that, theoretically, hydrogen peroxide could also be used for gas generation. If a low temperature hydrogen peroxide system were used instead of the existing systems, it would have one major advantage: lower oceanic pollution. The hydrazine system represents a potentially toxic release into the ocean system in the event of a leak or rupture of the hydrazine storage tank. This might occur accidentally or as a result of combat operations. In the event that the system is operated as intended, the releases are not nearly as toxic. Hydrogen peroxide on the other hand is already present in trace amounts in the ocean (Yuan & Shiller, 2001). The use of hydrogen peroxide would also eliminate toxic and corrosive effects

of carbohydrazide formation and would reduce complexity by eliminating heater/heating requirements on the propellant and gas generator (Wernimon *et al*, 2009)⁴⁹.

6.5.2 Practical Experience of EU Stakeholders with Alternatives

It is not clear to what extend the solid propellant gas generators are used in the EU; however, solid propellant systems appear to be available for implementation.

6.5.3 Limiting Factors for the Uptake of Alternatives

The key disadvantages of the solid propellant gas generator appear to be the increased volume of propellant needed and the higher exhaust gas temperatures.

6.6 Information on Similar Substances that may act as Substitutes

6.6.1 Substitution Scenarios

6.6.1.1 Replacement by Salts

The potential replacement of hydrazine by one or more of its salts has not been confirmed for the applications at the focus of this study (i.e. for applications that might be subject to authorisation under the REACH Regulation). For example, as discussed in Section 4.4.1, the choice between hydrazine and any of its salts in electrolytic/electroless metal deposition is defined by the presence of other anions in the plating bath, hence hydrazine cannot be simply replaced by one of its salts across all of its plating applications.

Among the applications outside the immediate scope of this study, there are indications that some salts of hydrazine may be used in its place for nuclear reactor waste processing. While some sources refer to the use of hydrazine as a reductant, other sources would suggest that its salts (sulphate or mononitrate) may be used. However, we have not received conclusive information from consultation to establish whether such interchangeability is valid.

In summary, in light of the available information, we cannot conclusively establish for which applications relevant to the EU which particular salts may act as alternatives for hydrazine (hydrate). The possibility cannot be excluded at this point but specific examples cannot be provided.

⁴⁹ Past investigations have indicated that the presence of relatively small amounts (ca. 100 ppm) of carbon dioxide impurity in hydrazine in contact with stainless steel can lead to significant metal corrosion and to an increase in the concentration of dissolved metal ions. The involvement of carbon dioxide in promoting stainless steel corrosion by hydrazine and the consequent increase in propellant decomposition rate has prompted the suggestion that certain transition metal complexes, involving ligands derived from hydrazine and carbon dioxide, may function as homogeneous catalysts for the decomposition of hydrazine. Carbon dioxide itself, which dissolves in hydrazine to give carbohydrazide (also known as carbazic acid), $2 N_2H_4 + CO_2 \rightarrow N_2H_5^+.N_2H_3CO_2^-$, is also claimed to be an effective catalyst in the corrosion process (Bellerby, 1982).

6.6.1.2 Interchangeability of Anhydrous and Hydrate Forms

This report explains that both the anhydrous and the hydrate form of hydrazine find uses in the EU. These two forms have different CAS Numbers but apparently share the same EC Number. Still, the available information suggests that the two forms have separate applications: while the anhydrous form is used exclusively in the aerospace and defence industries, the use of the hydrated form spans the synthesis, water, effluent and waste treatment, the production of metals, the purification of reagents and the manufacture of paints, inks and dyes (and potentially other less prominent applications which have not been confirmed). Literature sources indicate that some specific explosive mixtures may be produced with the anhydrous and some others with hydrated form, and there has also been a suggestion (in literature) that the anhydrous form may be used in synthesis processes where the presence of water is undesirable. However, we have not obtained evidence that such applications are of relevance to the EU.

6.6.1.3 Replacement by Derivatives

In light of the discussion in the earlier parts of Section 6, those substances that are related to hydrazine and could theoretically act as replacements for it include MMH, UDMH and carbohydrazide. These are further compared and discussed below.

6.6.2 Comparison on Hazard Characteristics and Toxicity of Hydrazine and Selected Substitutes

Table 6.12 presents a comparison of the hazard classification for hydrazine and for the three selected derivatives/substitutes. The information for hydrazine (using the CAS Number for the anhydrous form) and UDMH has been taken from Annex VI to Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of Dangerous Substances. For the other two substances, relevant entries are not available in the Annex and the information presented below was obtained from Safety Data Sheets available on the Internet.

Fable 6.12: Comparison of Hazard Classification of Hydrazine and Selected Hydrazine Derivatives								
Hydrazine (anhydrous)	MMH*	UDMH	Carbohydrazide					
R10: Flammable	R11: Highly flammable	R11: Highly flammable	R5: Heating may cause an explosion					
R23/24/25: Toxic by inhalation, in contact with skin and if swallowed	R26/27/28: Very toxic by inhalation, in contact with skin and if swallowed	R23/25: Toxic by inhalation and if swallowed	R20/21/22: Harmful by inhalation, in contact with skin and if swallowed					
R34: Causes burns	R34: Causes burns	R34: Causes burns						
R43: May cause sensitization by skin contact			R36/37/38: Irritating to eyes, respiratory system and skin					
R45: May cause cancer (Carc. Cat 2)	R45: May cause cancer	R45: May cause cancer (Carc. Cat. 2)						

Table 6.12: Comparison of Hazard Classification of Hydrazine and Selected Hydrazine Derivatives								
Hydrazine (anhydrous)	MMH*	UDMH	Carbohydrazide					
**	R46: May cause heritable genetic damage							
R50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment	R51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment	R51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment	R51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment					
T: Toxic C: Corrosive N: Dangerous for the environment	T: Toxic C: Corrosive F: Highly flammable	T: Toxic C: Corrosive F: Highly flammable N: Dangerous for the environment	Xn: Harmful N: Dangerous for the environment					
Source: ClassLab ¹	Source: Acros Organics ² Sigma Aldrich ³	Source: ClassLab ⁴	Source: Acros Organics ⁵					
Notes:		I	<u> </u>					
* For MMH, classification entries in Safety Data Sheets available online vary; this table presents the most 'severe' classifications given by suppliers								
** There are references i	n literature on potential m	utagenic effects of hydrazi	ne					
¹ <u>http://ecb.jrc.ec.europ</u> <u>3&subLang=EN</u>	¹ <u>http://ecb.jrc.ec.europa.eu/classification-labelling/clp/ghs/subDetail.php?indexNum=007-008-00-3&subLang=EN</u>							
² <u>https://fscimage.fisher</u>	sci.com/msds/39720.htm							
³ <u>http://www.chemblink</u>	.com/MSDS/MSDSFiles/60)-34-4 Sigma-Aldrich.pdf						
⁴ <u>http://ecb.jrc.ec.europ</u> <u>5&subLang=EN</u>	a.eu/classification-labellir	ng/clp/ghs/subDetail.php?u	<u>indexNum=007-012-00-</u>					
⁵ <u>http://search.be.acros</u> <u>field29.4=497187%29</u>	.com/physical?tg=29&sea 9+and+Field29.8=EN&for	rch=%28field29.9=10280 r=chemexper⊃=⟨	<u>42+or+</u> <u>z=</u>					

The key conclusions from the table could be:

- carbohydrazide is clearly less toxic than the other three substances and does not appear to have carcinogenic potential (yet it breaks down into hydrazine at high temperatures);
- both MMH and UDMH are highly flammable, while hydrazine is only flammable. Carbohydrazide does not pose a flammability hazard (and in dilute solutions the risk of explosion must be substantially low);
- hydrazine, MMH and UDMH may cause cancer and are toxic to the environment, although the aquatic toxicity of hydrazine could be more severe compared to the other two substances. Hydrazine does not have an EU mutagenicity classification, which MMH apparently is accompanied with in some commercial Safety Data Sheets.

However, there are references in literature to the potential mutagenic effects of hydrazine;

- hydrazine is a sensitiser, which the other three substances are not; and
- MMH is also very toxic through inhalation, skin contact and orally, while hydrazine and UDMH appear not to have such a severe toxic effect.

Sutton & Biblarz (2010) confirm that MMH is the most toxic hydrazine when inhaled and is a known animal carcinogen. The American Conference of Industrial Hygienists (ACGIH) recommends an 8h-TWA of 0.01 ppm. For UDMH, the ACGIH recommends an 8h-TWA of 0.01 ppm as well.

The National Academies (2000) indicate that the comparative toxicity of hydrazine, MMH and the symmetrical and asymmetrical isomers of dimethylhydrazine were reported by Jacobson *et al* (1955). Rats and mice exposed to hydrazine, and rats exposed to symmetrical dimethylhydrazine exhibited restlessness, dyspnoea, and convulsions with exophthalmos. Excessive salivation, vomiting, respiratory distress, and convulsions were reported for dogs exposed to UDMH as well as MMH. Fourteen-day mortality in three groups of dogs (three dogs per group) exposed for 4h to UDMH at concentrations of 24, 52, or 111 ppm were 0/3, 1/3, and 3/3, respectively. For rodents, estimated LC_{50} values for hydrazine, MMH, and UDMH are shown in **Table 6.13** (The National Academies, 2000).

Species	Hydrazine (ppm)	MMH (ppm)	UDMH (ppm)
Rat	570 (4 h)	74 (4 h)	252 (4 h)
Mouse	252 (4 h)	56 (4 h)	172 (4 h)
Hamster	ND	143 (4 h)	392 (4 h)

Jacobson *et al* (1955) noted that the toxic actions of hydrazine and its methylated derivatives were similar; all were found to be respiratory irritants and convulsants. However, MMH also induced severe intravascular haemolysis in dogs (The National Academies, 2000).

Witkin (1956) reported intravenous (i.v.), intraperitoneal (i.p.), and oral LD_{50} (lethal dose for 50% of the animals) values for mice and rats, and i.v. LD_{50} values for dogs. Similar to hydrazine, the route of administration had minimal effect on the LD_{50} within species. Generally, MMH appeared to be somewhat more toxic in mice than hydrazine and UDMH was less acutely toxic than hydrazine or the other hydrazine derivatives (The National Academies, 2000).

Relative to other forms of hydrazine, House (1964) reported UDMH to be less toxic to monkeys, rats, and mice. Mortalities over a 90-d inhalation exposure at 0.56 ppm (0.73 mg/m^3) were 20%, 98%, and 99% for monkeys, rats, and mice, respectively (The National Academies, 2000).

Table 6.14 presents a summary of the inhalation, oral and skin toxicity test results for hydrazine, MMH and UDMH, as presented in the ChemIDplus database. Test results are also available for routes such as i.v., i.p. and subcutaneous routes but these are not presented here. This table confirms the information presented above according to which MMH is the most toxic

of the three substances; UDMH appears to be somewhat less toxic than hydrazine. Only limited results (and none for the inhalation, oral and skin routes) were found for carbohydrazide from the same source. The available data would suggest a toxicity lower to that of hydrazine, as generally confirmed in literature discussing alternative oxygen scavengers. It should be noted that this toxicological information was collected from a single source and should be considered indicative rather than exhaustive.

Table 6.14: Comparison of Past Test Results on the Toxicity of Hydrazine, MMH and UDMH											
Hydrazine				MMH				UDMH			
Organism	Test Type	Route	Reported Dose	Organism	Test Type	Route	Reported Dose	Organism	Test Type	Route	Reported Dose
Mouse	LC ₅₀	Inhalation	330 mg/m ³ (4h)	Rat	LC ₅₀	Inhalation	64 mg/m ³ (4h)	Guinea pig	LC ₅₀	Inhalation	100 mg/m ³ (4h)
Rat	LC ₅₀	Inhalation	475 mg/m ³ (4h)	Mouse	LC ₅₀	Inhalation	105 mg/m ³ (4h)	Mouse	LC ₅₀	Inhalation	421 mg/m ³ (4h)
				Monkey	LC ₅₀	Inhalation	154 mg/m ³ (1h)	Rat	LC ₅₀	Inhalation	617 mg/m ³ (4h)
				Dog	LC ₅₀	Inhalation	180 mg/m ³ (1h)	Hamster	LC ₅₀	Inhalation	960 mg/m ³ (4h)
				Hamster	LC ₅₀	Inhalation	269 mg/m ³ (4h)	Dog	LC ₅₀	Inhalation	8,770 mg/m ³ (15m)
				Guinea pig	LC ₅₀	Inhalation	270 mg/m ³ (4h)				
Mouse	LD ₅₀	Oral	59 mg/kg	Hamster	LD ₅₀	Oral	22 mg/kg	Rat	LD ₅₀	Oral	122 mg/kg
Rat	LD ₅₀	Oral	60 mg/kg	Mouse	LD ₅₀	Oral	29 mg/kg	Mouse	LD ₅₀	Oral	155 mg/kg
	I			Rat	LD ₅₀	Oral	32 mg/kg				
Rabbit	LD ₅₀	Skin	91 mg/kg	Guinea pig	LD ₅₀	Skin	48 mg/kg	Dog	LD _{Lo}	Skin	301 mg/kg
Dog	LD _{Lo}	Skin	96 mg/kg	Rabbit	LD ₅₀	Skin	95 mg/kg	Rat	LD ₅₀	Skin	770 mg/kg
Guinea pig	LD ₅₀	Skin	190 mg/kg	Rat	LD ₅₀	Skin	183 mg/kg	Rabbit	LD ₅₀	Skin	1,060 mg/kg
	I	I	<u> </u>	Hamster	LD ₅₀	Skin	239 mg/kg	Guinea pig	LD ₅₀	Skin	1,329 mg/kg
Source: base	Source: based on information from the ChemIDplus Database, <u>http://chem.sis.nlm.nih.gov/</u>										

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ANNEX 1. OCCUPATIONAL EXPOSURE ESTIMATION ASSUMPTIONS

A1.1 Introduction

Some estimations of occupational exposure to hydrazine have been undertaken for certain uses of the substance, based on information presented in the report as well as expert judgement. The most relevant activities are:

- filling of (generally closed) systems, in which either anhydrous hydrazine or hydrazine hydrate is used; and
- metal (electroless) plating, assumed to take place in open systems.

The estimates for electroless plating are relatively uncertain because of a lack of specific information on the percentage of hydrazine in the baths used.

A1.2 Exposure from Use of Anhydrous Hydrazine

A1.2.1 Scenarios Considered

In uses as rocket propellant, fighter jet emergency power units and submarine rescue systems anhydrous hydrazine is used. These systems are closed systems. The potential exposure occurs due to transfer of the hydrazine into the system. We consider that, given the small amounts of propellant used in these applications, filling is undertaken from drums.

Inhalation exposure was estimated using the Advanced REACH Tool (ART)⁵⁰. The following situations have been assessed:

- pumping of anhydrous hydrazine from drums where the product contains >99% hydrazine (aerospace applications); and
- pumping of anhydrous hydrazine from drums where the product contains 70% hydrazine (fighter jet emergency power units).

A1.2.2 Estimates of Inhalation Exposure

The following parameters are assumed to apply:

- the distance of the source from the worker is conservatively chosen as within 1 meter;
- room temperature is chosen as the default temperature range for transfer;
- indoor use in rooms with a size of 300 m³ and a general ventilation of three air exchanges per hour are chosen as typical for industrial situations;
- transfer of liquid product is the typical activity class;

⁵⁰ Available here: <u>http://www.advancedreachtool.com/</u>.

- because of the known hazards of the substance, it is assumed that the filling is done submerged, through a small opening and the process is fully enclosed;
- as risk reduction measures, the use of both vapour recovery and additional fixed capturing hoods is assumed;
- specific drum pumping systems with vapour return exist and are seen as a reasonable option in these kinds of industries; and
- the duration of exposure is based on our understanding of the processes involved.

Exposure levels are estimated with and without the use of respiratory protective equipment (RPE) with a reduction effect of 90% for both the task and the full shift. The assumed effect of RPE is used as an indication of typical reduction. With more advanced RPE, such as equipment with an independent air supply, higher reduction effects can be achieved. For powered filtering devices incorporating helmets or hoods⁵¹, a reduction of 97.5% can be assumed (i.e. an assigned protection factor of 40, Brouwer *et al*, 2001). This would lead to exposure levels that are four times lower than those calculated with a reduction effect of 90%.

The upper end of the interquartile range of the 75th percentile is used as the reasonable worstcase estimate and the effect of RPE (90% reduction) is only assumed to apply during the task. **Table A1.1** shows the inputs and results of the estimates.

Table A1.1: Modelling Assumptions and Estimates of Inhalation Exposure during the Use of Anhydrous Hydrazine							
Parameter \ situation	Pumping from drum – anhydrous (>99%)	Pumping from drum – anhydrous (70%)					
Inputs							
Type of product	Liq	luid					
Vapour pressure (pure) (Pa)	2000						
Fraction in product (%)	100	70 (option 'main component' used in ART)					
Process temperature range	Room temperature (15 – 25 °C)						
Primary emission source < 1 meter of head of worker	Yes						
Activity class	Transfer of liquid products						
Activity subclass	Falling	liquids					
Situation (transfer of liquid product with flow of)	10 – 100 L/min						
Containment level	Handling that reduces contact be	etween product and adjacent air.					
Loading type	Submerge	ed loading					
Process fully enclosed	Y	es					
Proper cleaning and maintenance	Not relevant						

⁵¹ SCAPE (Self-contained Atmospheric Protective Ensemble) suits.

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Parameter \ situation	Pumping from drum – anhydrous (>99%)	Pumping from dru anhydrous (70%			
Work area	Ind	oors			
Room size	30	0 m^3			
General ventilation	3 air exchanges per hour				
Primary localised control	Vapour recovery system (80% effectiveness)				
Secondary localised control	Local exhaust ventilation: fixed capturing hood (90% effectiveness)				
Duration of activity (min)	15				
Results (mg/m ³)					
75 th percentile during task – no RPE	0.46	0.32			
Interquartile range during task – no RPE	0.23 – 0.90	0.16 - 0.64			
Reasonable worst case task – with RPE (90% reduction)	0.09	0.064			
Reasonable worst case full shift – no RPE during task	0.028	0.020			
Reasonable worst case full shift – with RPE during task	0.003	0.002			

A1.2.3 Estimates of Dermal Exposure

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Dermal exposure has been estimated with the ECETOC TRA v2 model⁵². For dermal exposure, the effect of local exhaust ventilation is not taken into account, as this is generally not considered to affect dermal exposure to liquids in transfer. For the transfer from drums, Process Category (PROC) 9 is used (Transfer of substance or preparation into small containers (dedicated filling line, including weighing). The effect of protective gloves is assumed to be a reduction of exposure by 90%. The inputs and resulting exposure estimates are presented in **Table A1.2**.

Table A1.2: Modelling Assumptions and Estimates of Dermal Exposure during the Use of Anhydrous Hydrazine					
Parameter \ situation	Pumping from drum – anhydrous (>99%)	Pumping from drum – anhydrous (70%)			

⁵² Available here: <u>http://www.ecetoc.org/tra</u>.

Parameter \ situation	Pumping from drum – anhydrous (>99%)	Pumping from drum - anhydrous (70%)	
Inputs		I	
Fraction in product (%)	100	70	
Process category (PROC)	9	9	
Results (mg/kg bw/day)			
Exposure of full product in µg/cm ²	1,000	1,000	
Exposed surface area (cm ²)	480	480	
Exposure to hydrazine - without PPE	6.86	4.80	
Exposure to hydrazine - with PPE	0.69	048	

A1.3 Exposure from Use of Hydrazine Hydrate in Closed Systems

A1.3.1 Transfer of Different Concentrations of Hydrazine Hydrate

In different uses, different concentrations of hydrazine hydrate can be used as input. To indicate the range of exposure this may result in, exposure estimates were made for three different starting concentrations: 100%, 55% and 5% hydrazine hydrate (effectively, 64%, 35% and 3% expressed as anhydrous hydrazine).

A1.3.2 Scenarios Considered

In uses as an intermediate, in water treatment or in other closed systems (e.g. precious metal precipitation), hydrazine is added to a closed system in either large or smaller volumes with higher or lower frequencies. Adding is done either via connection of pipelines (from large containers) or via drum pumps. Dedicated systems are expected to be used due to the hazardous properties of the substance.

Exposure may occur due to the activity of adding, in which case some opening of systems is required. Exposure estimates are made for the following activities:

- pumping of hydrazine hydrate (three different concentrations) from drums; and
- transfer of hydrazine hydrate (three different concentrations) from a tank truck.

A1.3.3 Estimates of Inhalation Exposure

The general assumptions for these estimates, which have been made with the ART model are the same as for pumping of anhydrous hydrazine. The only modification is the percentage of anhydrous hydrazine used. In relation to transfer from trucks, it is assumed that, although transfer to and from tank trucks often occurs outside, the worst-case situation would be indoors in a large hall. Therefore, this has been taken forward also for transfer from tank trucks. In addition, tank truck transfer of volatile very hazardous chemicals is often equipped with vapour return systems. This is assumed to be the case.

The results of the estimates for inhalation exposure are presented in Table A1.3.

ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

Parameter \ situation	Pumping hydrazine hydrate from drum		Tanker transfer – hydrazine hydrate						
	100%	55%	5%	100%	55%	5%			
Inputs		<u> </u>							
Type of product	Liquid								
Vapour pressure (pure) (Pa)	2000								
Fraction in product (%) [*]	64	35	3	64	35	3			
Process temperature range	Room temperature (15 – 25 °C)								
Primary emission source < 1 meter of head of worker	Yes								
Activity class	Transfer of liquid products								
Activity subclass	Falling liquids								
Situation (transfer of liquid product with flow of)	10 – 100 L/min 100 – 1000 L/min								
Containment level	Handling that reduces contact between product and adjacent air.								
Loading type	Submerged loading								
Process fully enclosed	Yes								
Proper cleaning and maintenance	Not relevant								
Work area	Indoors								
Room size	300 m ³								
General ventilation	3 air exchanges per hour								
Primary localised control	Vapour recovery system (80% effectiveness)								
Secondary localised control	Local exhaust ventilation: fixed capturing hood (90% effectiveness)								
ANNEX XV – IDENTIFICATION OF HYDRAZINE AS SVHC

Parameter \ situation	Pumping hydrazine hydrate from drum			Tanker transfer – hydrazine hydrate		
	100%	55%	5%	100%	55%	5%
Duration of activity (min)	15			180		
Results (mg/m ³)						
75 th percentile during task – no RPE	0.29	0.16	0.014	0.87	0.48	0.041
Interquartile range during task – no RPE	0.15 - 0.58	0.081 - 0.32	0.007 - 0.027	0.44 – 1.7	0.24 - 0.95	0.021 - 0.082
Reasonable worst-case task – with RPE (90% reduction)	0.058	0.032	0.003	0.17	0.095	0.008
Reasonable worst-case full shift – no RPE during task	0.018	0.010	0.001	0.64	0.36	0.031
Reasonable worst-case full shift – with RPE during task	0.002	0.001	< 0.001	0.064	0.036	0.003
Source: TNO calculations						

A1.3.4 Estimates of Dermal Exposure

Dermal exposure has been estimated with the ECETOC TRA model. As before, for dermal exposure, the effect of local exhaust ventilation is not taken into account as this is generally not considered to affect dermal exposure to liquids in transfer. For the transfer from drums Process Category (PROC) 9 is used (Transfer of substance or preparation into small containers (dedicated filling line, including weighing), while for the transfer from tanker trucks PROC 8b (Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities) is used. In both cases, the effect of protective gloves is assumed to be a reduction of exposure by 90%. The inputs and resulting exposure estimates are presented in **Table A1.4**.

Parameter \ situation	Pumping hydrazine hydrate from drum			Tanker transfer – hydrazine hydrate		
	100%	55%	5%	100%	55%	5%
Inputs						1
Fraction in product (%)	64	35	3	64	35	3
Process category (PROC)		9			8b	
Results (mg/kg bw/day)				I		
Exposure of full product in $\mu g/cm^2$	1,000	1,000	1,000	1,000	1,000	1,000
Exposed surface area (cm ²)	480	480	480	480	480	480
Exposure to hydrazine - without PPE	4.39	2.40	0.21	4.39	2.40	0.21
Exposure to hydrazine - with PPE	0.44	0.24	0.021	0.44	0.24	0.021

A1.4 Exposure from Use of Hydrazine Hydrate in Open Systems

A1.4.1 Scenarios Considered

Applications of hydrazine hydrate where its use may take place in open systems are plating operations (typically electroless, although possibilities for electrolytic plating also exist).

For the modelling of occupational exposure, it is assumed that hydrazine hydrate rather than a salt is generally used. To use the substance in the process, this has to be mixed into the relevant bath (or in a premix that is added to the bath). Exposures from mixing will probably not be very frequent, but no information on frequency and methods of mixing hydrazine in this process is available.

It is assumed that, for preparing a solution for electroless plating containing hydrazine, an amount of 5% hydrazine hydrate (i.e. 3% expressed as anhydrous hydrazine) is pumped from a

drum into a bath. Local exhaust ventilation is expected to be available, but the system is not expected to be as contained as in some other transfer situations mentioned for transfer into closed systems.

The concentration of hydrazine in an electroless plating bath is generally low. As discussed in Section 4.4.1, the concentration of hydrazine or its salts in electroless baths ranges between 0.3 g/L hydrazine to 15 g/L hydrazine chloride (Lloret, 2010). Where hydrazine derivatives (chloride or sulphate) are used, the exposure for preparation of the bath is due to the use of the derivative and not hydrazine itself. However, in the use of the bath the actual exposure is to hydrazine, because the substance is expected to dissociate in the bath. To account for the different concentrations of hydrazine or its derivatives, a reasonable worst-case concentration of 2% hydrazine in a bath is assumed, which is high compared to the values mentioned by Lloret (2010). As an opposite 'extreme', a concentration of 0.01% will be used to indicate potential exposure for baths with a very low level of hydrazine.

A1.4.2 Estimates of Inhalation Exposure

Inhalation exposure is estimated with the ART model. The following specific assumptions are made:

- electroless baths are used at elevated temperatures;
- it is assumed that workers do, in generally, not work close to the bath that contains hydrazine, but that exposure could be for a full shift (480 minutes);
- a room size of 300 m³ and an air exchange rate of three air exchanges per hour are assumed for industrial situations;
- for the preparation of the bath or premix of hydrazine solution, it is assumed that fixed capturing hoods are available, while canopy (receiving) hoods are assumed for the baths themselves; and
- the surface area from which the substance can evaporate is assumed to be between 0.3 and 1 m^2 . Some baths may be larger, but it is assumed that they will then be partly covered with a lid during the actual operation as much as possible.

Table A1.5: Modelling Assumptions and Estimates of Inhalation Exposure during the Preparation and Use of Electroless Plating Baths containing Hydrazine Hydrate						
Parameter \ situation	Preparation of bath	Operation of bath (2%)	Operation of bath (0.01%)			
Input						
Type of product	Liquid	Liquid	Liquid			
Vapour pressure (pure) (Pa)	2000	2000	2000			
Fraction in product (%)	3	2	0.01			
Process temperature range	Room temperature $(15 - 25 \degree C)$	Hot processes (50 – 150 °C)				

The inputs to the model and the inhalation exposure estimates are given in Table A1.5.

Table A1.5: Modelling Assumptions and Estimates of Inhalation Exposure during thePreparation and Use of Electroless Plating Baths containing Hydrazine Hydrate					
Parameter \ situation	Preparation of bath	Operation of bath (2%)	Operation of bath (0.01%)		
Primary emission source < 1 meter of head of worker	Yes	No			
Activity class	Liquid transfer	Activities with open liquid surfaces or open reservoirs			
Activity subclass	Falling liquids	Activities with relatively undisturbed surfaces (no aerosol formation)			
Situation (transfer of liquid product with flow of)	10 – 100 L/min	Not relevant			
Situation (open surface area of)	Not relevant	$0.3 - 1 \text{ m}^2$			
Containment level	Open process	Open process			
Loading type	Splash loading	g Not relevant			
Process fully enclosed	No				
Proper cleaning and maintenance	Yes				
Work area	Indoors				
Room size	300 m ³				
General ventilation	3 air exchanges per hour				
Primary localised control	Local exhaust ventilation: fixed capturing hood	Local exhaust ventilation: canopy hood (receiving hood)			
Secondary localised control	None	None			
Duration of activity (min)	15	480			
Results (mg/m^3)					
75 th percentile during task – no RPE	0.68	0.85	0.004		
Interquartile range during task – no RPE	0.35 – 1.4	0.43 – 1.7	0.002 - 0.009		
Reasonable worst case task – with RPE (90% reduction)	0.14	0.17	< 0.001		

Table A1.5: Modelling Assumptions and Estimates of Inhalation Exposure during thePreparation and Use of Electroless Plating Baths containing Hydrazine Hydrate					
Parameter \ situation	Preparation of bath	Operation of bath (2%)	Operation of bath (0.01%)		
Reasonable worst case full shift – no RPE during task	0.044	1.7	0.009		
Reasonable worst case full shift – with RPE during task	< 0.001	0.17	< 0.001		
Source: TNO calculations					

A1.4.3 Estimates of Dermal Exposure

Dermal exposure is estimated with the ECETOC TRA model. For dermal exposure, the situation of PROC25 (handling of hot metal) is considered to be most similar to the situation of working with hot electroless plating baths.

Table A1.6: Modelling Assumptions and Estimates of Dermal Exposure during the Preparation and Use of Electroless Plating Baths containing Hydrazine Hydrate						
Parameter \ situation	Preparation of bath	Use of bath (2%)	Use of bath (0.01%)			
Inputs						
Fraction in product (%)	3	2	0.01			
Process category (PROC)	9	25				
Results (mg/kg bw/day)						
Exposure of full product in µg/cm ²	1,000	10	10			
Exposed surface area (cm ²)	480	1980	1980			
Exposure to hydrazine - without PPE	4.46	0.006	< 0.001			
Exposure to hydrazine - with PPE	0.45	< 0.001	< 0.001			
Source: TNO calculations						

ANNEX 2. CONFIDENTIAL INFORMATION ON MARKETS AND USES

ANNEX 3. CONFIDENTIAL INFORMATION ON RELEASES

ANNEX 4. CONFIDENTIAL INFORMATION ON ALTERNATIVES