

# **Draft Assessment Report (DAR)**

**- public version -**

**Initial risk assessment provided by the rapporteur Member State  
the Netherlands for the existing active substance**

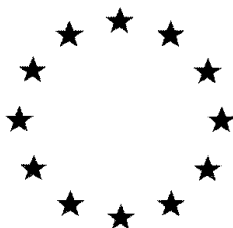
**SODIUM HYPOCHLORITE**

**of the fourth stage of the review programme  
referred to in Article 8(2) of Council Directive 91/414/EEC**

**Volume 3, Annex B, part 1, B1 - B5**

**February 2009**

# **European Commission**



## **SODIUM HYPOCHLORITE**

**VOLUME 3**

**Annex B**

**Rapporteur Member State: The Netherlands**

**May 2008**

Draft Assessment Report and Proposed Decision of the Netherlands prepared in the context of  
the possible inclusion of sodium hypochlorite in Annex I of Council Directive 91/414/EEC

**CONTENTS**

<b>B.1</b>	<b>Identity</b>	<b>1</b>
B.1.1	Identity of active substance (Annex IIA 1 and 3.1)	1
B.1.2	Identity of the plant protection product (Annex IIIA 1)	1
B.1.3	References relied on	1
<b>B.2</b>	<b>Physical and chemical properties</b>	<b>2</b>
B.2.1	Physical and chemical properties of the active substance (Annex IIA 2)	2
B.2.2	Physical, chemical and technical properties of the plant protection product	6
B.2.3	Summary and evaluation of physical-chemical properties	14
B.2.4	References relied on	14
<b>B.3</b>	<b>Data on application and further information</b>	<b>17</b>
B.3.1	Data on application relevant to the active substance (Annex IIA 3.1 to 3.6)	17
B.3.2	Data on application relevant to the plant protection product (Annex IIIA 3)	18
B.3.3	Summary of data on application	19
B.3.4	Further information on the active substance (Annex IIA 3.7 to 3.9)	21
B.3.5	Further information of the plant protection product (Annex IIIA 4)	26
B.3.6	References relied on	28
<b>B.4</b>	<b>Proposals for classification and labelling</b>	<b>29</b>
B.4.1	Proposals for the classification and labelling of the active substance (Annex IIA 10)	29
B.4.2	Proposals for the classification and labelling of preparations (Annex IIIA 12.3 and 12.4)	30
B.4.3	References relied on	30
<b>B.5</b>	<b>Methods of analysis</b>	<b>31</b>
B.5.1	Analytical methods for formulation analysis (Annex IIA 4.1; Annex IIIA 5.1)	31
B.5.2	Analytical methods (residue) for plants, plant products, foodstuffs of plant and animal origin, feeding stuffs (Annex IIA 4.2.1 and Annex IIIA 5.2)	32
B.5.3	Analytical methods (residue) soil, water, air (Annex IIA 4.2.2 to 4.2.4; Annex IIIA 5.2)	32
B.5.4	Analytical methods (residue) for body fluids and tissues (Annex IIA 4.2.5; Annex IIIA 5.2)	34
B.5.5	Evaluation and assessment	34
B.5.6	References relied on	35

<b>B.6</b>	<b>Toxicology and metabolism</b>	<b>37</b>
B.6.1	Absorption, distribution, excretion and metabolism (toxicokinetics) (Annex IIA 5.1)	39
B.6.2	Acute toxicity including irritancy and skin sensitisation (Annex IIA 5.2)	42
B.6.3	Short-term toxicity (Annex IIA 5.3)	60
B.6.4	Genotoxicity (Annex IIA 5.4)	68
B.6.5	Long-term toxicity and carcinogenicity studies (Annex IIA 5.5)	72
B.6.6	Reproductive toxicity (Annex IIA 5.6)	79
B.6.7	Neurotoxicity / Delayed neurotoxicity (Annex IIA 5.7)	87
B.6.8	Further toxicological studies (Annex IIA 5.8)	87
B.6.9	Medical data and information (Annex IIA 5.9)	90
B.6.10	Summary of mammalian toxicology and proposed ADI, AOEL, ARFD and drinking water limit (Annex IIA 5.10)	92
B.6.11	Acute toxicity including irritancy and skin sensitization of preparations (Annex IIIA 7.1)	101
B.6.12	Dermal absorption (Annex IIIA 7.3)	101
B.6.13	Toxicological data on non active substances (Annex IIIA 7.4)	101
B.6.14	Exposure data (Annex IIIA 7.2)	101
B.6.15	References relied on	108
<b>B.7</b>	<b>Residue data</b>	<b>109</b>
B.7.1	Metabolism, distribution and expression of residues in plants (Annex IIA 6.1 and Annex IIIA 8.1)	109
B.7.2	Metabolism, distribution and expression of residues in livestock (Annex IIA 6.2 and Annex IIIA 8.1)	110
B.7.3	Definition of the residue (Annex IIA 6.7; Annex IIIA 8.6)	110
B.7.4	Use pattern	110
B.7.5	Identification of critical GAPs	111
B.7.6	Residues resulting from supervised trials (Annex IIA 6.3; Annex IIIA 8.2)	113
B.7.7	Effects of industrial processing and/or household preparation (Annex IIA 6.5; Annex IIIA 8.4)	113
B.7.8	Livestock feeding studies (Annex IIA 6.4; Annex IIIA 8.3)	113
B.7.9	Residues in succeeding or rotational crops (Annex IIA 6.6; Annex III 8.5)	113
B.7.10	Proposed pre-harvest intervals for envisaged uses, or withholding periods, in the case of post-harvest uses (Annex IIA 6.8; Annex IIIA 8.7)	113
B.7.11	Community MRLs and MRLs in EU Member States (Annex IIIA 12.2)	113
B.7.12	Proposed EU MRLs and justification for the acceptability of those MRLs (Annex IIA 6.7; Annex IIIA 8.6)	113

B.7.13	Proposed EU Import tolerances and justification for the acceptability of those residues	114
B.7.14	Basis for differences, if any, in conclusions reached having regard to established or proposed CAC MRLs	114
B.7.15	Estimates of potential and actual dietary exposure through diet and other means (Annex IIA 6.9; Annex IIIA 8.8)	114
B.7.16	Summary and evaluation of residue behaviour (Annex IIA 6.10; Annex IIIA 8.9)	114
B.7.17	References relied on	114
<b>B.8</b>	<b>Environmental Fate and Behaviour</b>	<b>115</b>
B.8.1	Route and rate of degradation in soil (Annex IIA 7.1.1 and Annex IIIA 9.1.1)	115
B.8.2	Adsorption, desorption and mobility in soil (IIA 7.1.2, 7.1.3, IIIA 9.1.2)	115
B.8.3	Predicted environmental concentrations in soil (PECs) (Annex IIIA 9.1.3)	115
B.8.4	Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2.1/9.2.3)	115
B.8.5	Impact on water treatment procedures (Annex IIIA 9.2.2)	119
B.8.6	Predicted environmental concentrations in surface water, in sediment and in groundwater (PEC <sub>sw</sub> , PEC <sub>sed</sub> , PEC <sub>gw</sub> ) (Annex IIIA 9.2.1, 9.2.3)	121
B.8.7	Fate and behaviour in air (Annex IIA 7.2.2; Annex IIIA 9.3)	122
B.8.8	Predicted environmental concentrations in air (PEC <sub>a</sub> ) (Annex IIIA 9.3)	125
B.8.9	Definition of the residue (Annex IIA 7.3)	125
B.8.10	References relied on	126
<b>B.9</b>	<b>Ecotoxicology</b>	<b>128</b>
B.9.1	Effects on birds (IIA 8.1; IIIA 10.1)	130
B.9.2	Effects on aquatic organisms (Annex IIA 8.2; Annex IIIA 10.2)	131
B.9.3	Effects on other terrestrial vertebrates (Annex IIIA 10.3)	153
B.9.4	Effects on bees (Annex IIA 8.3.1; Annex IIIA 10.4)	153
B.9.5	Effects on other arthropod species (Annex II A 8.3.2; Annex III A 10.5)	154
B.9.6	Effects on earthworms (Annex IIA 8.4; Annex IIIA 10.6.1)	154
B.9.7	Effects on other soil non-target macro-organisms (Annex IIIA 10.6.2)	154
B.9.8	Effects on soil non-target micro-organisms (Annex IIA 8.5; Annex IIIA 10.7)	154
B.9.9	Effects on other non-target organisms (flora and fauna) believed to be at risk (Annex IIA 8.6)	154
B.9.10	Effects on biological methods of sewage treatment (Annex IIA 8.7)	154
B.9.11	References relied on	156

<b>Appendix 1</b>	<b>Part 1: Standard terms and abbreviations</b>	<b>157</b>
	<b>Part 2: Organisations and publications</b>	<b>164</b>
	<b>Part 3: Preparation (formulation) types and codes</b>	<b>167</b>
<b>Appendix 2</b>	<b>Specific terms and abbreviations</b>	<b>171</b>

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

## **B.1 Identity**

### **B.1.1 Identity of the active substance (Annex IIA 1 and 3.1)**

All points of Annex IIA, Section 1, point 1 are addressed in Volume 1, Level 1.

### **B.1.2 Identity of the plant protection product (Annex IIIA 1)**

All points of Annex IIIA, Section 1, point 1 are addressed in Volume 1, Level 1.

### **B.1.3 References relied on**

Confidential references are listed in Volume 4, Annex C.

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## B.2 Physical and chemical properties

### B.2.1 Physical and chemical properties of the active substance (Annex IIA 2)

The physical and chemical properties of sodium hypochlorite as manufactured in a 10 - 12% active chlorine solution in water are given below. When available information on GLP, purity or method used is indicated. In most cases this information was not available.

#### B.2.1.1 Melting point (IIA 2.1)

-20 to -30°C (RAR, 2007).

Crystallization of sodium hypochlorite occurs at -25°C (IUCID, 2000).

Sodium hypochlorite solutions will freeze at different temperatures depending upon strength (T.C.I., 2006, pamphlet 96)

Weight Percent NaOCl	Freezing Point (°C)
2	-2.2
4	-4.4
6	-7.5
8	-10.0
10	-13.9
12	-19.4
14	-25.6
16	-26.9

#### B.2.1.2 Boiling point (IIA 2.1)

96 - 120 °C, decomposition in chlorate and chloride. (RAR, 2007)

#### B.2.1.3 Temperature of decomposition or sublimation (IIA 2.1)

Decomposition rate doubles at every raise of temperature by 5.5°C. Above 35°C decomposition is very rapid (RAR, 2007)

#### B.2.1.4 Density (IIA 2.2)

1.23 g/cm<sup>3</sup> at 25°C (RAR, 2007) for a 15% available chlorine solution.

Empirical formula's exist to estimate the density of the solution, depending on the concentration (assumption: the content of sodium hydroxide (or the pH) is high enough for a stable solution).

$$\text{density (g/ml)} = 0.0161 * [\text{NaOCl, \%w/w}] + 0.9974$$

$$\text{density (g/ml)} = 0.0169 * [\text{Cl}_2, \%w/w] + 0.9974$$



Another way to estimate is the discussion below. (T.C.I., 2006, pamphlet 96).

The specific gravities for the solutions shown in Table 2-2 were calculated using the equation below. In this calculation, a correction factor, developed from experimental data, is added to the measured specific gravity of sodium hypochlorite solutions that contain no excess sodium hydroxide. Good agreement has been found between the measured density for hypochlorite solutions containing excess caustic soda and the calculated density using this equation.

$$\text{density NaOCl Sol. w/Excess NaOH} = \text{density NaOCl Sol. w/o Excess NaOH} + (0.00135 \times \text{gpl excess NaOH})$$

<b>Table 2-2. Specific Gravity of Sodium Hypochlorite Solutions With Various Levels of Excess NaOH @ 20°C</b>						
gpl Available Chlorine	gpl Excess Sodium Hydroxide (NaOH)					
	0	2	4	6	8	10
6.0	1.082	1.085	1.087	1.090	1.093	1.096
8.0	1.107	1.110	1.112	1.115	1.118	1.121
10.0	1.132	1.135	1.137	1.140	1.143	1.146
12.0	1.157	1.160	1.162	1.165	1.168	1.171
14.0	1.180	1.183	1.185	1.188	1.191	1.194
15.0	1.192	1.195	1.197	1.200	1.203	1.205
16.0	1.204	1.207	1.209	1.212	1.215	1.218
18.0	1.227	1.230	1.232	1.235	1.238	1.241
20.0	1.249	1.252	1.254	1.257	1.260	1.263

#### **B.2.1.5 Vapour pressure (IIA 2.3)**

1.74 to 2.0 kPa.s at 20°C (RAR, 2007)

This is the vapour pressure of water itself. Sodium hypochlorite will not evaporate easily. The only compounds that are potential volatile are chlorine and hypochlorous acid. See also point B.2.1.18.

#### **B.2.1.6 Volatility, Henry's law constant (IIA 2.3)**

Not applicable. Sodium hypochlorite will not evaporate from water; only chlorine or hypochlorous acid can potentially evaporate.

#### **B.2.1.7 Appearance: physical state (IIA 2.4)**

Liquid

#### **B.2.1.8 Appearance: colour (IIA 2.4)**

Clear, colourless to greenish and/or yellowish

#### **B.2.1.9 Appearance: odour (IIA 2.4)**

Characteristic smell, chlorine

**B.2.1.10 Spectra (IIA 2.5)**

Not applicable

**B.2.1.11 Solubility in water (IIA 2.6)**

Miscible (RAR, 2007)

293 g/L at 0°C (Merck, 2001)

Chlorine is only slightly soluble in water. When it reacts with pure water, a weak solution of hydrochloric and hypochlorous acids is formed.

**B.2.1.12 Solubility in organic solvents (IIA 2.7)**

Not applicable (sodium hypochlorite reacts with several organic solvents, Urban, 1999)

**B.2.1.13 Partition coefficient (IIA 2.8)**

Not applicable

**B.2.1.15 Hydrolysis (IIA 2.9)**

Bleach decomposition is 2nd order with respect to NaOCl concentration. The second order rate law predicts that diluting the NaOCl by a factor of 2 should decrease the rate of NaOCl decomposition by a factor of 4. However, actual decomposition data for sodium hypochlorite solutions shows that a factor of 2 decrease in NaOCl concentration results in an approximate factor of 5 decrease in the rate of decomposition. This is because of the effect on the decomposition rate by the decrease in the total ionic concentration of the solution. Since the dilution of a bleach solution not only decreases the NaOCl concentration but also decreases the concentration of all the ions in the solution (chloride ions, the chlorate ions, hydroxide ions, etc.), the total ionic strength is also decreased and further reduces the decomposition rate (T.C.I., 2006, pamphlet 96).

**B.2.1.16 Photochemical degradation (IIA 2.9)**

A sodium hypochlorite solution is very sensitive to light. Direct sunlight may cause rearrangement and decomposition resulting in the formation of chlorate and oxygen. The presence of isocyanuric acid in solution reduces this sensitivity to a great extent (RAR, 2007).

Half life of a 10 to 15% available chlorine solution will be reduced 3 to 4 times by sunlight. (IUCLID, 2000)

**B.2.1.17 Quantum yield (IIA 2.9)**

Not applicable

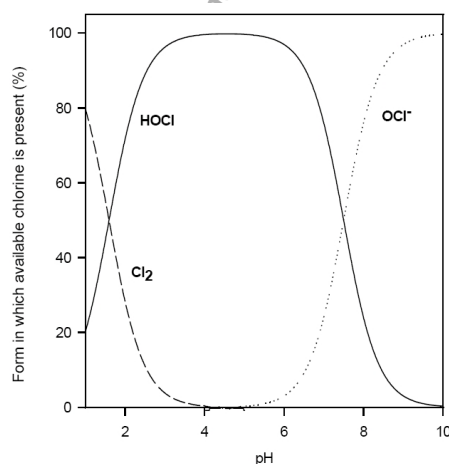
**B.2.1.18 Dissociation constant (pKa) (IIA 2.9)**

The pKa of hypochlorous acid is approximately 7.5 at 25°C (WHO, 2000).

In solution the sodium hypochlorite is in equilibrium with chlorine and hypochlorous acid. The equilibrium is temperature and pH dependant (RAR, 2007)

Species in aqueous solution as a function of pH

There are three species of chlorine in equilibrium in water: gaseous chlorine, hypochlorous acid (HOCl, also a gas at room temperature and pressure), and  $\text{ClO}^-$ . An example of the distribution between them as a function of pH is shown in figure below (example for a 0.1 M  $\text{Cl}_2$  solution). For example, at pH 7.5 half of the chlorine is active as HOCl and half is available as  $\text{ClO}^-$ . The pH of commercial solutions is above 11 and the only species effectively present is  $\text{ClO}^-$ . At pH12, the equilibrium  $\text{OCl}^-/\text{HOCl}$  is  $10^{19.53}$  ( $K_a=2.90 \cdot 10^{-8}$  at 25°C). The amount of hypochlorous acid decreases as pH and temperature increase. At pH 7.0 70% is HOCl whereas at pH 8.0 80% is  $\text{ClO}^-$  when the temperature is 25°C. Therefore in freshwater (characteristic pH range of 6.5-7.2) the dominant form is the more toxic HOCl while at estuarine pH's (7.5-8.2) the reverse is true. At pH values above 4.0,  $\text{Cl}_2$  does not exist. Temperature also affects the equilibrium between HOCl and hypochlorite, but to a much lesser extent than pH, with the ionization content (pKa) for HOCl decreasing from 7.75 at 5°C to 7.63 at 15°C and 7.54 at 25°C (RAR, 2007).

**B.2.1.19 Stability in air (thermal stability) (IIA 2.10)**

Not applicable.

**B.2.1.19 Photochemical oxidative degradation (IIA 2.10)**

Not applicable.

**B.2.1.20 Flammability (IIA 2.11)**

No flammable properties are expected, as this is an aqueous solution of an inorganic molecule.

Non flammable (method: DIN 51584) (RAR, 2007)

**B.2.1.20 Auto-flammability (IIA 2.11)**

No flammable properties are expected as this is a aqueous solution of an inorganic molecule

**B.2.1.21 Flash point (IIA 2.12)**

No flammable properties are expected as this is a aqueous solution of an inorganic molecule

**B.2.1.22 Explosive properties (IIA 2.13)**

Not explosive as solution (ECB classification of sodium hypochlorite), however the anhydrous solid sodium hypochlorite is very explosive (Merck, 2001).

**B.2.1.23 Oxidising properties (IIA 2.15)**

Sodium hypochlorite is a strong oxidising agent. However it is not oxidising in the sense of EEG method A17 (solids) or A21 (liquids) (ECB classification; RAR, 2007).

**B.2.1.24 Surface tension (IIA 2.14)**

Not applicable

**B.2.2 Physical, chemical and technical properties of the plant protection products (Annex IIIA 2)**

The plant protection product is the same as the active substance.

**B.2.2.1 Appearance: physical state (IIIA 2.1)**

Liquid.

**B.2.2.2 Appearance: colour (IIIA 2.1)**

Clear, colourless to greenish and/or yellowish

**B.2.2.3 Appearance: odour (IIIA 2.1)**

Characteristic smell, chlorine

**B.2.2.4 Explosive properties (IIIA 2.2)**

Not explosive as solution (ECB classification for sodium hypochlorite), however the anhydrous solid sodium hypochlorite is very explosive (Merck, 2001).

**B.2.2.5 Oxidising properties (IIIA 2.2)**

Sodium hypochlorite is a strong oxidising agent. However it is not oxidising in the sense of EEG method A17 (solids) or A21 (liquids) (ECB classification; RAR, 2007)

**B.2.2.6 Flammability (IIIA 2.3)**

No flammable properties are expected as this is a aqueous solution of an inorganic molecule

**B.2.2.7 Auto-Flammability (IIIA 2.3)**

No flammable properties are expected as this is a aqueous solution of an inorganic molecule

**B.2.2.8 Flash point (IIIA 2.3)**

No flammable properties are expected as this is a aqueous solution of an inorganic molecule

**B.2.2.9 Acidity/alkalinity (IIIA 2.4)**

See pH, B.2.2.10.

**B.2.2.10 pH (IIIA 2.4)**

The pH determination is very difficult because of the high pH and e.g. special electrodes are required.

Exact pH is also very dependent on the sodium hydroxide concentration and varies much.

The pH of a 0.5 to 5.0 % NaClO solution ranged from 11.98 to 12.9 (pH was measured with a pH meter at 25°C) (Guerisoli, 1998). However for other products the pH can be somewhat different, as the solution is stabilized by adding a certain excess amount of sodium hydroxide.

In the proposed use the sodium hypochlorite (10 - 12%) is diluted 800 - 930 fold. No data is available for the pH of this dilution. However starting with a pH of 11 – 12, a thousand fold dilution theoretically will reduce the pH to 8 – 9.

**B.2.2.11 Surface tension (IIIA 2.5)**

To determine the surface tension of the solutions, a tensiometer (Fischer Scientific, Surface Tensiomat 21) was used.

The surface tension of a 0.5 to 5.0 % NaClO solution was 74 – 76 dynes/cm at 25°C and is therefore equal to water (Guerisoli, 1998). The surface tension of distilled water is 72 dyne/cm at 25 °C (Wikipedia).

**B.2.2.12 Viscosity (IIIA 2.6)**

Determined with an Ostwald viscometer, based on the flow time of a liquid from a bulb through a capillary when subjected to its own weight. The flow time of the solution was compared with the time of a known viscosity liquid (water), thus, the viscosity of the solutions were obtained. Ten repetitions were made for each experimental group.

The viscosity of a 0.5 to 5.0 % NaClO solution ranged from 0.956 to 1.110 mPa.s at 25°C and is therefore equal to water (Guerisoli, 1998).

Dynamic viscosity at 20°C: 2.6 mPa.s (concentration sodium hypochlorite not given, but expected to be in the range 10 - 12% available chlorine). (IUCLID, 2000).

**B.2.2.13 Relative density (IIIA 2.6)**

See density, B.2.1.4.

**B.2.2.14 Bulk (tap) density (IIIA 2.6)**

Not applicable.

**B.2.2.15 Storage stability for 14 days at 54°C (IIIA 2.7)**

See shelf life, B.2.2.16.

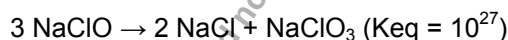
**B.2.2.15 Storage stability for 7 days at 0°C (IIIA 2.7)**

See shelf life, B.2.2.16.

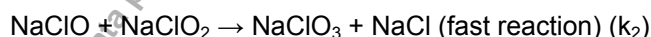
**B.2.2.16 Shelf life (IIIA 2.7)**

From (RAR, 2007):

In concentrated sodium hypochlorite solutions, the content of available chlorine decreases because NaClO tends to disproportionate to chloride and chlorate ions. The reaction is:



It is the resultant of two reactions: a slow one with formation of chlorite and a fast one with formation of chlorate by reaction between chlorite and hypochlorite.



The first reaction (that produces chlorite) controls the reaction rate producing chlorate. The formation rate of chlorate, at room temperature and pH = 11, is very slow. The process is dependant on the time, temperature, impurities, pH and concentration of the sodium hypochlorite solution. Also light can decompose hypochlorite solutions.

Time Dependence

At constant temperature the inverse of the active product concentration is a linear function of the time. A solution dosed at 150 g/l available chlorine which is kept away from sunlight and at constant 15°C, loses 1/6 of its concentration within less than 3 months. In diluted hypochlorite solutions the losses are minor.

From (T.C.I., 2006, pamphlet 96):

However, studies of sodium hypochlorite solutions have shown that the decomposition rate increases by a factor in the range of 3 to 4 times for every 10°C for solutions in the range of 5% to 16% by weight of sodium hypochlorite, which is not unusual. The table below shows the relative change in the decomposition rate for a 15 weight percent sodium hypochlorite solution over a temperature range of 25°C to 45°C. The table cannot be used to estimate the absolute decomposition rate.

Application use: sodium hypochlorite stored at 15°C will decompose 14 times slower than sodium hypochlorite when stored at 35°C. Storage of sodium hypochlorite at low temperatures such as 15°C will greatly reduce decomposition of sodium hypochlorite for any practical application in strength ranging from 10 – 16% by weight sodium hypochlorite. With decrease temperatures to 5 °C and no heavy metal contamination, the decomposition of the sodium hypochlorite will be virtually eliminated.

Rate Constants for Sodium Hypochlorite Decomposition					
NaOCl %w/w					
Temperature	15.89%	13.46%	10.82%	7.93%	4.74%
55°C	250	189	138	98.2	65.5
45°C	80.7	58.7	43.9	30.2	19.3
35°C	23.1	17.0	12.2	8.43	5.45
25°C	6.33	4.68	3.22	2.19	1.58
15°C	1.65	1.15	0.8	0.53	0.30

#### pH Dependence

Hypochlorite should not be added to an unbuffered medium, because at low pH, the following secondary reactions could occur. In acid media under pH 4 hypochlorite will be transformed to gaseous chlorine.

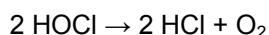


Between pH 4 and 11, both  $\text{ClO}^-$  and  $\text{HOCl}$  are present with the latter being much more active. This pH will be obtained when all the sodium hydroxide present in the hypochlorite solution has been carbonated. Degradation of  $\text{HOCl}$  is more rapid than the degradation of  $\text{ClO}^-$ .

if pH <6, the main reaction is:  $2 \text{HClO} \rightarrow 2 \text{HCl} + \text{O}_2$

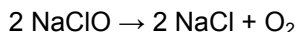
if pH >6, the main reaction is:  $3 \text{NaClO} \rightarrow \text{NaClO}_3 + 2 \text{NaCl}$

Hypochlorous acid ( $\text{HClO}$ ) is very unstable and it suddenly decomposes with formation of oxygen:



#### Dependence upon Impurities

Sodium hypochlorite can decompose to oxygen according to the following reaction:



The decomposition reaction is a bimolecular one and requires an activation energy of 113.3 kJ/mol (26.6 kcal/mol). Although it is slower than the chlorate formation reaction, it is catalysed by trace amounts of metallic impurities. The strongest decomposition catalysts to oxygen are: Co, Ni and Cu; whereas Fe and Mn are weaker catalysts. To avoid decomposition of commercial hypochlorite solutions, these metals must be reduced as much as possible. Generally, their elimination occurs mechanically by filtering as their solubility is reduced during the hypochlorite production step. Salts such as sodium chloride, sodium carbonate and sodium chlorate have only a very low influence on reaction rate within the range of concentration where they are normally present. Their influence on reaction rate is only remarkable in some particular cases (e.g. diluted High Grade Sodium hypochlorite where NaCl content is highly reduced because of the specific production process). Sodium hydroxide does not influence the reaction rate if its concentration is greater than  $10^{-3}$  M (0.04 g/l).

#### Light Dependence

The sodium hypochlorite solution is very sensitive to light. Direct sunlight may cause rearrangement and decomposition resulting in the formation of chlorate and oxygen. The presence of isocyanuric acid in solution reduces this sensitivity to a great extent.

#### Temperature Dependence

The influence of temperature is very high: the decomposition rate doubles if the temperature increases by  $\sim 5.5^\circ\text{C}$  (see rate constant table at time dependency). If temperature is more than  $35^\circ\text{C}$ , the decomposition reactions are very rapid:



In every case, the temperature of the solution must be below  $55^\circ\text{C}$  in order to prevent a sudden decomposition of the hypochlorite. The more stable solutions are those of low hypochlorite concentration, with a pH of 11 and low iron, copper, and nickel content, stored in the dark at low temperature.

The exact stability of the 10 – 12 % solution is unknown. The notifier is asked to provide data on stability of the 10 – 12 % solution.

#### **B.2.2.17 Wettability (IIIA 2.8)**

Not applicable.

#### **B.2.2.18 Persistent foaming (IIIA 2.8)**

Not applicable.



**B.2.2.19    Suspensibility (IIIA 2.8)**

Not applicable.

**B.2.2.20    Suspension stability (IIIA 2.8)**

Not applicable.

**B.2.2.21    Dilution stability (IIIA 2.8)**

Dilution of the sodium hypochlorite solution may be useful because it enhances the stability (shelf life, B.2.2.16) or required for the application. It is important to use clean water, and to ensure that the pH stays above 11.9 (shelf life, B.2.2.16). If the pH is below 11.9 consider adding additional sodium hydroxide to the solution. The amount of caustic soda to be added can be estimated using a small volume of the diluted sodium hypochlorite solution.

In the proposed use the sodium hypochlorite (10 - 12%) is diluted 800 - 930 fold.

**B.2.2.22    Dry sieve test (IIIA 2.8)**

Not applicable.

**B.2.2.23    Wet sieve test (IIIA 2.8)**

Not applicable.

**B.2.2.24    Particle size distribution (IIIA 2.8)**

Not applicable.

**B.2.2.25    Content of dust/fines (IIIA 2.8)**

Not applicable.

**B.2.2.26    Attrition and friability (IIIA 2.8)**

Not applicable.

**B.2.2.27    Emulsifiability, re-emulsifiability and emulsion stability (IIIA 2.8)**

Not applicable.

**B.2.2.28    Stability of dilute emulsion (IIIA 2.8)**

Not applicable.

**B.2.2.28    Flowability (IIIA 2.8)**

Not applicable.

**B.2.2.29    Stability of dilute emulsion (IIIA 2.8)**

Not applicable.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must be granted on the basis of this document.

**B.2.2.30 Pourability (rinsibility) (IIIA 2.8)**

Not applicable.

**B.2.2.31 Dustability (IIIA 2.8)**

Not applicable.

**B.2.2.32 Adherence and distribution to seeds (IIIA 2.8)**

Not applicable.

**B.2.2.33 Physical compatibility of tank mixes (IIIA 2.9)**

See B.2.2.34, Chemical compatibility of tank mixes

**B.2.2.34 Chemical compatibility of tank mixes (IIIA 2.9)**

Sodium hypochlorite is not chemically compatible with a number of compounds. In the table below the materials are mentioned, with the possible results on mixing.

Incompatible Material	Mixing May Result In
<p>Acids, Acidic Compounds and Acid Based Cleaning Compounds such as:</p> <ul style="list-style-type: none"> <li>- Alum (Aluminum Sulfate)</li> <li>- Aluminum Chloride</li> <li>- Ferrous or Ferric Chloride</li> <li>- Ferrous or Ferric Sulfate</li> <li>- Chlorinated Solutions of Ferrous Sulfate</li> <li>- Hydrochloric Acid (HCl)</li> <li>- Sulfuric Acid</li> <li>- Hydrofluoric Acid</li> <li>- Fluorosilicic Acid</li> <li>- Phosphoric Acid</li> <li>- Brick and Concrete Cleaners</li> </ul>	<ul style="list-style-type: none"> <li>- Release of chlorine gas, may occur violently.</li> </ul>
<p>Chemicals and Cleaning Compounds containing ammonia such as:</p> <ul style="list-style-type: none"> <li>- Ammonium Hydroxide</li> <li>- Ammonium Chloride</li> <li>- Ammonium Silicofluoride</li> <li>- Ammonium Sulfate</li> <li>- Quaternary Ammonium Salts (Quats)</li> </ul>	<ul style="list-style-type: none"> <li>- Formation of explosive compounds.</li> <li>- Release of chlorine or other noxious gases.</li> </ul>
<p>Organic Chemicals and Chemical Compounds such as:</p> <ul style="list-style-type: none"> <li>- Solvents and Solvent Based Cleaning Compounds</li> <li>- Fuels and Fuel Oils</li> <li>- Amines</li> <li>- Propane</li> <li>- Organic Polymers</li> <li>- Ethylene Glycol</li> <li>- Insecticides</li> <li>- Methanol</li> </ul>	<ul style="list-style-type: none"> <li>- Formation of chlorinated organic compounds.</li> <li>- Formation of explosive compounds.</li> <li>- Release of chlorine gas, may occur violently.</li> </ul>
<p>Metals such as:</p> <ul style="list-style-type: none"> <li>- Copper</li> <li>- Nickel</li> <li>- Cobalt</li> <li>- Iron</li> </ul> <p>Avoid piping and material handling equipment containing stainless steel, aluminum, carbon steel or other common metals.</p>	<ul style="list-style-type: none"> <li>- Release of oxygen gas, generally does not occur violently. Could cause overpressure/rupture of a closed system.</li> </ul>
Hydrogen Peroxide	<ul style="list-style-type: none"> <li>- Release of oxygen gas, may occur violently.</li> </ul>
<p>Reducing agents such as:</p> <ul style="list-style-type: none"> <li>- Sodium Sulfite</li> <li>- Sodium Bisulfite</li> <li>- Sodium Hydrosulfite</li> <li>- Sodium Thiosulfate</li> </ul>	<ul style="list-style-type: none"> <li>- Evolution of heat, may cause splashing or boiling.</li> </ul>

### B.2.3 Summary and evaluation of physical-chemical properties

#### B.2.3.1 Active substance

Sodium hypochlorite is produced as a liquid with 10-12% available chlorine. The content of the solution is expressed as available chlorine as in solution several compounds are formed and the equilibrium is dependent on pH and temperature.

Sodium hypochlorite reacts with a variety of compounds. It will not evaporate from water. The 10 – 12% available chlorine solution is instable and will slowly decompose. Stability is dependent on concentration available chlorine, pH, temperature and other storage conditions.

#### B.2.3.2 Plant protection product(s)

See B.2.3.1.

The formulation is the same as the active substance.

### B.2.4 References relied on

#### References for the active substance

Annex point/ reference no.	Author(s)	Year	Title Company, report no. Source (where different from company) GLP or GEP status (where relevant) Published or not	Data Protection Claimed Y/N	Owner
IIA 2	RAR (unknown)	2007	RISK ASSESSMENT REPORT FOR SODIUM HYPOCHLORITE, DRAFT November 2007 Italy non GLP Published (via ECB website)	N	ECB
IIA 2.1; 2.2; 2.9	T.C.I.	2006	Pamphlet 96, Sodium Hypochlorite Manual The Chlorine Institute inc. Edition 3, April 2006 Non GLP Published ( <a href="http://www.chlorineinstitute.org/">http://www.chlorineinstitute.org/</a> )	N	The Chlorine Institute
IIA 2.1; 2.9	EU-ECB	2000	IUCLID Dataset, sodium hypochlorite 19 Feb 2000 non GLP Published (via ECB website)	N	ECB

Annex point/ reference no.	Author(s)	Year	Title Company, report no. Source (where different from company) GLP or GEP status (where relevant) Published or not	Data Protection Claimed Y/N	Owner
IIA 2.4; 2.5	Guerisoli	1998	GUERISOLI, D.M.Z.; SILVA, R.S.; PÉCORA, J.D. Evaluation of some physico-chemical properties of different concentrations of sodium hypochlorite solutions. <i>Braz. Endod. J.</i> 3(2): 21-3, 1998.  Non GLP Published	N	-
IIA 2.6; 2.13	Merck	2001	Merck Index 13 <sup>th</sup> edition, 2001 Merck Research Laboratories, Whitehouse Station, New York, USA Senior Editor M.J. O'Neil non GLP Published	N	Merck
IIA 2.7	Urban	1999	Bretherick's handbook of reactive chemical hazards, 6 <sup>th</sup> edition editor: P.G. Urban Butterworth-Heinemann, Linacre house, Jordan hill, Oxford OX2 *DP, Engeland published	N	BH
IIA 2.9	WHO	2000	Environmental Health Criteria 216, DISINFECTANTS AND DISINFECTANT BY-PRODUCTS Version November 30, 2000 Published non-GLP	N	WHO
IIA 2.13; 2.15	ECB	n.r.	For classification via ECB website	N	ECB

**References for the plant protection product**

<b>Annex point/ reference no.</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title</b> <b>Company, report no.</b> <b>Source (where different from company)</b> <b>GLP or GEP status (where relevant)</b> <b>Published or not</b>	<b>Data Protection Claimed Y/N</b>	<b>Owner</b>
IIIA 2	RAR (unknown)	2007	RISK ASSESSMENT REPORT FOR SODIUM HYPOCHLORITE, DRAFT November 2007 Italy non GLP Published (via ECB website)	N	ECB
IIIA 2.2	Merck	2001	Merck Index 13 <sup>th</sup> edition, 2001 Merck Research Laboratories, Whitehouse Station, New York, USA Senior Editor M.J. O'Neil non GLP Published	N	Merck
IIIA 2.2	ECB	n.r.	for classification via ECB website	N	ECB
IIIA 2.5	Unknown	Unknown	Wikipedia on internet, English version Published	N	Wikipedia
IIIA 2.6	EU- ECB	2000	IUCLID Dataset, sodium hypochlorite 19 Feb 2000 non GLP Published (via ECB website)	N	ECB
IIIA 2.6	Guerisoli	1998	GUERISOLI, D.M.Z.; SILVA, R.S.; PÉCOR, J.D. Evaluation of some physico-chemical properties of different concentrations of sodium hypochlorite solutions. <i>Braz. Endod. J.</i> 3(2): 21-3, 1998. Non GLP Published	N	-
IIIA 2.7	T.C.I.	2006	Pamphlet 96, Sodium Hypochlorite Manual The Chlorine Institute inc. Edition 3, April 2006 Non GLP Published ( <a href="http://www.chlorineinstitute.org/">http://www.chlorineinstitute.org/</a> )	N	The Chlorine Institute

### **B.3 Data on application and further information**

#### **B.3.1 Data on application relevant to the active substance (Annex IIA 3.1 to 3.6)**

##### **B.3.1.1 Function (Annex IIA 3.1)**

Sodium hypochlorite acts as a disinfectant in the application to mushroom crops for the control of Bacterial Blotch.

##### **B.3.1.2 Nature of the effects on harmful organisms (Annex IIA 3.2.1)**

Chlorine kills pathogens such as bacteria and viruses by breaking the chemical bonds in their molecules. Disinfectants that are used for this purpose consist of chlorine compounds which can exchange atoms with other compounds, such as enzymes in bacteria and other cells. When enzymes come in contact with chlorine, one or more of the hydrogen atoms in the molecule are replaced by chlorine. This causes the entire molecule to change shape or fall apart. When enzymes do not function properly, a cell or bacterium will die. ([www.lenntech.com](http://www.lenntech.com))

Bacterial blotch is caused by *Pseudomonas tolaasii*, which is known to occur frequently in peat and chalk as a natural inhabitant. At certain times of the year, in particular in the spring and autumn, epidemics of bacterial blotch occur. This disease results in brown staining of the mushroom caps which are either heavily downgraded (light infections) or unsaleable. Although *Pseudomonas tolaasii* is omnipresent in mushroom composts, it is important to keep levels below the threshold levels that result in spoilage symptoms. Mushroom growers have used sodium hypochlorite for many years in order to control bacterial blotch, which is effective on the cap tissue of the mushroom by reducing the level of blotch organisms that are present.

##### **B.3.1.3 Translocation in plants (Annex IIA 3.2.2)**

The product is applied up till bud formation of the mushrooms, and reacts very quickly, therefore translocation in plants is not relevant for this use

##### **B.3.1.4 Field of use (Annex IIA 3.3)**

Horticulture.

##### **B.3.1.5 Pests controlled and crops protected (Annex IIA 3.4)**

Sodium hypochlorite acts as a disinfectant in the application to mushroom crops for the control of Bacterial Blotch.

**B.3.1.6 Mode of action (Annex IIA 3.5.1)**

Chlorine acts as a powerful disinfectant when used either on its own, as sodium hypochlorite or as calcium hypochlorite. Added to water in minute quantities, it quickly kills bacteria and other microbes. Chlorine-based disinfection has a long history: the first time bleach was used to disinfect water was in 1897 to combat a typhoid outbreak in Maidstone, Kent (UK). Chlorine kills pathogens such as bacteria and viruses by breaking the chemical bonds in their molecules. Disinfectants that are used for this purpose consist of chlorine compounds which can exchange atoms with other compounds, such as enzymes in bacteria and other cells. When enzymes come in contact with chlorine, one or more of the hydrogen atoms in the molecule are replaced by chlorine. This causes the entire molecule to change shape or fall apart. When enzymes do not function properly, a cell or bacterium will die.  
(www.lenntech.com)

**B.3.1.7 Information relevant to the formation of active metabolites or degradation products (Annex IIA 3.5.2-3.5.3)**

Other than the formation of hypochloric acid there are no active metabolites or degradation products.

**B.3.1.8 Information on the possible occurrence of the development of resistance or cross-resistance (Annex IIA 3.6)**

The non specific action of the chlorine means that resistance to such a substance is most unlikely. There are no reports of resistance.

**B.3.2 Data on application relevant to the plant protection product (Annex IIIA 3)****B.3.2.1 Field of use (Annex IIIA 3.1)**

See section B.3.1.4.

**B.3.2.2 Effects on harmful organisms (Annex IIIA 3.2)**

See section B.3.1.2 and B.3.1.3.

**B.3.2.3 Pests controlled and crops protected (Annex IIIA 3.3)**

See section B.3.1.5.



**B.3.2.4 Minimum waiting periods or other precautions between last application and sowing or planting of succeeding crops. Limitations on choice of succeeding crops (Annex IIIA 3.8)**

Mushrooms appear in flushes, starting about 18 days after casing. Farmers try not to water mushrooms any larger than pea size i.e. they water in between flushes and may apply three or four on consecutive days and then go without for 7/8 days until the flush has been picked off. Sodium hypochlorite is stated to be quickly inactivated once it makes contact with the highly organic casing layer.

Therefore no waiting periods are necessary.

**B.3.2.9 Proposed instructions for use as printed, or to be printed, on labels (Annex IIIA 3.9)**

No information submitted. The notifier is asked to provide proposed instructions for use as printed on the label.

**B.3.3 Summary of data on application**

Intended uses are summarized in table B.3.3-1.

Table B.3.3-1 Summary of representative uses evaluated (sodium hypochlorite)

Crop and/ or situation	Member State or Country	Product name	F G or I (b)	Pests or Group of pests controlled (c)	Preparation		Application				Application rate per treatment (for explanation see the text in front of this section)			PHI (days)	Remarks
					Type (d-f)	Conc. of as (i)	method kind (f-h)	growth stage & sea- son (j)	number (max) (k)	interval between applications (min)	g as/hL min – max (l)	water L/ha min – max	g as/ha min – max (l)		
(a)															
Mushrooms	EU	Sodium hypo- chlorite	I	Bacterial blotch caused by Pseudomonas as tolaasii	10 – 12% available chlorine	In irrigation water applied by watering tree	From appearance of mushrooms on beds until mushrooms are pea size	40 <sup>A</sup>	1 day	31.5 Na- ClO ≈ 30 g available Cl <sub>2</sub>	10,000	3150 NaClO ≈ 3000 g available Cl <sub>2</sub>	1 <sup>B</sup>	<sup>A</sup> 40 applications per year (assuming 10 cultivation cycles per year and 3-4 applications per cycle)  <sup>B</sup> A PHI of 1 day was proposed by the notifier. However, in practice the PHI will be longer.	
(a) For crops, the EU and Codex classifications (both) should be taken into account; where relevant, the use situation should be described (e.g. fumigation of a structure)							(i) g/kg or g/L. Normally the rate should be given for the active substance (according to ISO) and not for the variant in order to compare the rate for same active substances used in different variants (e.g. fluoroxypry). In certain cases, where only one variant is synthesised, it is more appropriate to give the rate for the variant (e.g. benthialcarb-isopropyl).								
(b) Outdoor or field use (F), greenhouse application (G) or indoor application (I)							(j) Growth stage at last treatment (BBCH Monograph, Growth Stages of Plants, 1997, Blackwell, ISBN 3-8263-3152-4), including where relevant, information on season at time of application								
(c) e.g. biting and sucking insects, soil born insects, foliar fungi, weeds							(k) Indicate the minimum and maximum number of application possible under practical conditions of use								
(d) e.g. wettable powder (WP), emulsifiable concentrate (EC), granule (GR)							(l) The values should be given in g or kg whatever gives the more manageable number (e.g. 200 kg/ha instead of 200 000 g/ha or 12.5 g/ha instead of 0.0125 kg/ha)								
(e) GCPF Codes - GIFAP Technical Monograph No 2, 1989							(m) PHI - minimum pre-harvest interval								
(f) All abbreviations used must be explained															
(g) Method, e.g. high volume spraying, low volume spraying, spreading, dusting, drench															
(h) Kind, e.g. overall, broadcast, aerial spraying, row, individual plant, between the plant-type of equipment used must be indicated															

**B.3.4 Further information on the active substance (Annex IIA 3.7 to 3.9)****B.3.4.1 Recommended methods and precautions concerning handling, storage, transport or fire (Annex IIA 3.7)****B.3.4.1.1 Handling**

Do not breathe dust, mist, or vapour. Do not get in eyes, on skin, or on clothing. Use only in a chemical fume hood.

**B.3.4.1.2 Storage**

Do not store in direct sunlight. Store in a tightly closed container. Store in a dry area. Corrosives area. Keep refrigerated. (Store below 4°C). Keep separated from combustible and reducing substances, acids, food and feedstuffs (IPSC, 1999).

**B.3.4.1.3 Transport information**

Shipping Name	HYPOCHLORITE SOLUTIONS
Hazard Class	8
UN Number	UN1791
Packing Group	II, III
USCG CHRIS Code	SHP
USCG Compatibility Group	5 Caustics
IMO Pollution Category	C
IMO Hazard code	S/P

**B.3.4.1.4 Fire-fighting measures**

Use Powder, water spray, foam or carbon dioxide.

In case of fire: keep drums, etc., cool by spraying with water.

**B.3.4.2 Procedures for destruction or decontamination (Annex IIA 3.8)**

From (IPCS, 1999):

SPILLS: Ventilation. Collect leaking and spilled liquid in sealable containers as far as possible. Then wash away with plenty of water. Do NOT absorb in saw-dust or other combustible absorbents. Personal protection: complete protective clothing including self-contained breathing apparatus. Do NOT let this chemical enter the environment.

From (T.C.I., 2006, pamphlet 96):

## SPILLS

Whenever there is an imminent or actual spill of sodium hypochlorite your company Spill Control Plan must be immediately activated. Each spill of sodium hypochlorite should be handled by taking into account the nature and circumstances of that spill. Items that may be included in a spill plan include:

- Evacuation of all unnecessary personal from the area. The first responsibility of personal in the area should be to their own safety. They should take no action that would endanger themselves or others. Their next concern should be to keep other personal and the possible effected community safe. These actions would include any necessary evacuation of the effect area, and to denial entry to the spill area.
- Mitigation of the spill should start as soon as responders have equipped themselves and determined the source of the spill and what actions should be taken to stop therelease.
- Responders should contain the spilled material in the smallest possible area. Diking should be used to contain the spill if not in a containment area. Do not allow the bleach to enter sewers, streams, or unpaved land. Avoid contamination of contained material with acidic materials since this would result in a release of chlorine gas.
- Absorption can be used to clean up a sodium hypochlorite spill. If absorbents are used to soak up a spill, avoid sawdust and other combustible materials. Certify in advance that the absorbent can be safely used with sodium hypochlorite solutions. Note: The spill is now a solid waste and may be more difficult to disposal of in a solid form.
- Dilution of spilled sodium hypochlorite is an option if the spilled product can be diluted to the point where it is no longer a danger to personal or the environment. For larger spills this may require very large amounts of water.

## RECOVERY OF SPILLED MATERIAL

Recovery of contained spilled material should be given first priority, keeping in mind that the material is most likely contaminated in some way. Recovered material could be reused, or neutralized, pH adjusted and recovered in an approved process.

Absorb spill with inert material (e.g. vermiculite, sand or earth), then place in suitable container.

## DISPOSAL AND NEUTRALIZATION OF SODIUM HYPOCHLORITE SOLUTIONS

Disposal of significant volumes of aqueous solutions of sodium hypochlorite may require both reduction of the active chlorine followed by pH adjustment before discharging the liquid to any sanitary discharge system or receiving body of water. The issue should be discussed with the local authority and/or plant management first. The reason for the neutralization is the sodium hypochlorite can seriously disrupt sewage or other treatment plant operations resulting in failure of the biological processes at the sewage plant (extreme cases) or disruption of chemical treatment processes. In addition, waste streams containing sodium hypochlorite may come into contact with acidic conditions and chlorine gas may be released.

Sodium hypochlorite can be treated either in a batch operation or a continuous system. After neutralization of the spill the remaining material still may need to be pH adjusted, possibly in place, diluted and/or flushed with water, or removed as a liquid and solid material for proper disposal. This should be coordinated with the local environmental regulating agency.

**WARNING: Lowering the pH of a liquid bleach solution without first reducing the hypochlorite ion to chloride ion could result in the release of chlorine gas.**

All of the neutralization reactions progress relatively quickly. Destruction of all available chlorine can be confirmed by adding 3% hydrogen peroxide to a waste sample. If the sample fizzes, then free chlorine remains in the waste. By-product salts may also accumulate in the form of sulfates and chlorides that can cause corrosion problems. Also, there may be a notable shift in the pH value results and control of the reactions is relatively complicated since the endpoint of the neutralization cannot be measured with simple instrumentation methods.

**CAUTION: These reactions may produce heat, this must be taken into account!**

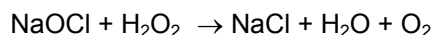
**IMPORTANT: Neutralizing materials of any kind should never be used on skin or eyes unless directed to do so by qualified medical personnel.**

#### Neutralization Chemicals

Neutralization reactions can be controlled using available chlorine titrations or oxidation/reduction potential (ORP) measurements. It is important to have adequate equipment and/or process systems and operating procedures to handle neutralization reactions and to always read and follow information contained in the MSDS for each of the neutralization chemicals including proper personal protective equipment.

#### Hydrogen Peroxide

One of the chemicals suitable for the reduction of hypochlorite ion available chlorine in sodium hypochlorite is hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), less than 35% concentration. The chemical reaction is as follows:



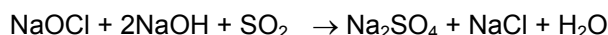
The sodium hypochlorite reacts spontaneously with the hydrogen peroxide and the resulting salt solution is adjusted for pH before discharge. The oxygen is vented to atmosphere at a safe point of discharge. An advantage of using hydrogen peroxide is the only end products are salt and water.

This reaction can easily be done on a batch basis in one tank with neutralization of the bleach first and pH adjustment second. On a continuous system, the solution is neutralized in a reactor vessel in the first step and then the pH is adjusted downstream in a second reactor. The hydrogen peroxide is added in the first tank and acid is added to the second with the appropriate ORP and pH control systems.

### Sulfur Dioxide

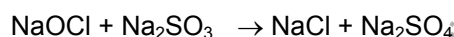
**WARNING:** Sulfur dioxide (SO<sub>2</sub>) is a corrosive gas and a safety program must be developed. The use of sulfur dioxide to neutralize sodium hypochlorite may result in release of gaseous chlorine if the pH is allowed to drop too low; a release of gaseous SO<sub>2</sub> may also result. Therefore, it is important to control the pH until all hypochlorite ions is destroyed and to be sure sulfur dioxide can no longer be released. Sulfur dioxide can be used for the reduction of available chlorine in sodium hypochlorite.

The chemical reaction is as follows:



### Sodium Sulfite

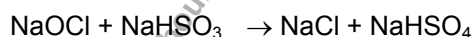
Sodium sulfite can be used for the reduction of available chlorine in sodium hypochlorite. The chemical reaction is as follows:



Small spills of standing sodium hypochlorite have been neutralized using sodium sulfite applied to the spill. This method has been used to neutralize spills on roadways, bar ditches, and in parking lots. This method should be covered with the local environmental regulating agency in the review of the Spill Control Plan.

### Sodium Bisulfite

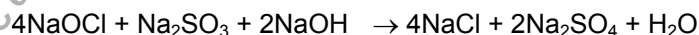
Sodium bisulfite can be used for the reduction of available chlorine in sodium hypochlorite. The chemical reaction is as follows:



Sodium bisulfite has been used to neutralize the available chlorine in bleach solutions. This reaction can be more vigorous than the other neutralizing chemicals listed. Appropriate personal protective equipment (PPE) and engineering controls should be used. This method should be covered with the local environmental regulating agency in the review of the Spill Control Plan.

### Sodium Thiosulfate

Sodium thiosulfate can be used for the reduction of available chlorine in sodium hypochlorite. The chemical reaction is as follows:



Sodium thiosulfate has been used to neutralize the available chlorine in bleach solutions. This reaction requires that caustic soda be added in addition to the thiosulfate. This reaction can generate less heat than some of the other neutralizing agents but can also produce significant quantities of solids.

Appropriate personal protective equipment (PPE) and engineering controls should be used. This method should be covered with the local environmental regulating agency in the review of the Spill Control Plan.

From (T.C.I., 2006, pamphlet 96):

#### WASTE

Hypochlorite solutions released during a spill may be considered as a hazardous waste depending on the pH and/or state regulations. Employees whose responsibility it is to clean up such spills should be trained to do so. Applicable training (OSHA or NFPA) for these employees would depend upon the extent of their duties during such a release.

#### **B.3.4.3 Emergency measures in case of an accident (Annex IIA 3.9)**

##### Personal precautions

Ventilation. Complete protective clothing including self-contained breathing apparatus.

##### Environmental precautions

Do NOT let this chemical enter the environment.

##### Clean up methods

See B.3.4.2.

##### Procedures for decontamination of water

Contaminated water must be contained. See instructions on MSDS.

##### First aid measures

Have the product container, label or MSDS with you when calling an emergency number, a poison control centre or physician, or going for treatment.

Inhalation	Fresh air, rest. Half-upright position. Refer for medical attention
Ingestion	Rinse mouth. Do NOT induce vomiting. Give water or milk. Refer for medical attention.
Skin contact	First rinse with plenty of water for 15 minutes, remove contaminated clothes and rinse again. Refer for medical attention.
Eye contact	First rinse with plenty of water for 15 minutes (remove contact lenses if easily possible), then take to a doctor.

#### **B.3.4.4 Summary of further information and assessment**

Information supplied addresses methods for handling the active substance.

**B.3.5 Further information on the plant protection product (Annex IIIA 4)****B.3.5.1 Packaging and compatibility on the preparation with proposed packaging materials (Annex IIIA 4.1)**

From (T.C.I., 2006, pamphlet 96):

Relatively few materials of construction can withstand the highly reactive nature of sodium hypochlorite. Improper selection of materials may result in damage to equipment and contamination of the product. As a general rule, do not allow metals (except for titanium and tantalum) to come in contact with sodium hypochlorite.

The materials listed below are examples of materials of construction that are compatible with sodium hypochlorite solutions and may be used alone or as linings for non-compatible materials of construction.

- PVDF (fluorinated polyvinylidene)
- PTFE (polytetrafluoroethylene)
- titanium
- ethylene propylene rubber
- 100% chlorobutyl rubber
- polypropylene
- PVC (polyvinyl chloride)
- CPVC (chlorinated polyvinyl chloride)
- FRP (fiberglass-reinforced plastic with compatible resin and cure system)
- poly dicyclopentadiene

**B.3.5.2 Procedures for cleaning application equipment (Annex IIIA 4.2)**

Not required. Cleaning of used equipment can be by rinsing with sufficient water.

**B.3.5.2.1 Application equipment**

Concentrate is diluted using a diluter or large volume tank & pump. Chlorinated water is applied with a watering tree (a movable tube based irrigation system). The volume applied would depend upon water requirement but would generally not exceed 1 litre per m<sup>2</sup> of bed surface. (Compost depth is about 9/10 inches (up to 30 cm) with about 2 inch (5 cm) depth of casing on top).

**B.3.5.3 Re-entry periods, necessary waiting periods or other precautions to protect man, livestock and the environment (Annex IIIA 4.3)****Pre-harvest intervals**

A pre-harvest interval of 1 day is recommended, though the interval between last application and harvest is more than a couple of days.



**Re-entry period for livestock to areas to be grazed**

Not applicable, because intended use crops are not grazed by livestock.

**Re-entry periods for man to crops, buildings or treated areas**

No re-entry period is considered necessary.

**Withholding periods for animal feedingstuffs**

Not applicable, use is not intended on animal feeding stuffs.

**Waiting period between application and handling treated products**

Refer to “Re-entry periods for man to crops, building or treated areas” above.

**Waiting periods between last application and sowing or planting succeeding crops**

There are no restrictions for succeeding crops.

**Information on any specific agricultural, plant health or environmental conditions under which the preparation may not be used**

None.

**B.3.5.4 Recommended methods and precautions concerning handling, storage, transport or fire (Annex IIIA 4.4)**

See B.3.4.

**B.3.5.5 Summary of further information and assessment**

Information supplied addresses methods for handling the formulation.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

**B.3.6 References relied on****References for the active substance**

<b>Annex point/ reference no.</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title</b> <b>Company, report no.</b> <b>Source (where different from company)</b> <b>GLP or GEP status (where relevant)</b> <b>Published or not</b>	<b>Data Protection Claimed Y/N</b>	<b>Owner</b>
IIA 3.8	IPCS	1999	International Chemical Safety cards, Sodium hypochlorite (solution, active chlorine>10%) No. ICSC 1119 October 19, 1999 Published (internet) non-GLP	N	IPCS
IIA 3.8	T.C.I.	2006	Pamphlet 96, Sodium Hypochlorite Manual The Chlorine Institute inc. Edition 3, April 2006 Non GLP Published ( <a href="http://www.chlorineinstitute.org/">http://www.chlorineinstitute.org/</a> )	N	The Chlorine Institute

**References for the plant protection product**

<b>Annex point/ reference no.</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title</b> <b>Company, report no.</b> <b>Source (where different from company)</b> <b>GLP or GEP status (where relevant)</b> <b>Published or not</b>	<b>Data Protection Claimed Y/N</b>	<b>Owner</b>
IIIA 4.1	T.C.I.	2006	Pamphlet 96, Sodium Hypochlorite Manual The Chlorine Institute inc. Edition 3, April 2006 Non GLP Published ( <a href="http://www.chlorineinstitute.org/">http://www.chlorineinstitute.org/</a> )	N	The Chlorine Institute

WARNING: This document forms part of an EC evaluation of data submitted in support of a registration. It should not be read in isolation. Registration must not be granted on the basis of this document.

## B.4 Proposals for classification and labelling

### B.4.1 Proposals for the classification and labelling of the active substance (Annex IIA 10)

Justified proposals for classification and labelling of the active substance sodium hypochlorite (aqueous solution containing 10 – 12% w/w available chlorine) according to Directive 67/548/EEC are listed below.

#### Physical chemical properties

Hazard symbol: none  
Indication of danger: none  
Risk phrases: R31 "Contact with acids liberates toxic gas"  
Safety phrases: none

Justification for the proposal: identical to the ECB classification.

#### Human health effects

Hazard symbol : C  
Indication of danger : corrosive  
Risk phrases : R34 "Causes burns"  
Safety phrases : S1/2 "Keep locked up and out of the reach of children"  
: S26 "In case of contact with eyes, rinse immediately with plenty of water and seek medical advice"  
: S28 "After contact with skin, wash immediately with plenty of water"  
: S36/37/39 "Wear suitable protective clothing, gloves and eye/face protection"  
: S45 "In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)"

#### Justification for the proposal:

The proposal is based on the RAR for sodium hypochlorite, and is identical to the ECB classification, 29<sup>th</sup> ATP (However, several additional safety phrases are proposed. ECB classification: S1/2, S28 and S45).

#### Specific limits:

Concentration  $\geq 10\%$  : C R34

Concentration  $\geq 5\%$  and  $< 10\%$  : Xi R36/38

The C&L Technical Group at the 15-18 March 2005 Meeting, decided to maintain the above classification.

Theoretically pure sodium hypochlorite should be classified as “harmful for ingestion” (Xn, R22) on the basis of the oral LD<sub>50</sub> data. This classification does not apply to solutions as their concentration is always below 25%.

### Ecotoxicological effects

Hazard symbol:	N
Indication of danger:	“Dangerous for the environment”
Risk phrases:	R50 “Very toxic to aquatic organisms” R53 “May cause long-term adverse effects in the aquatic environment”
Safety phrases:	S29 “Do not empty into drains” S56 “Dispose of this material and its container to hazardous or special waste collection point” S60 “This material and its container must be disposed of as hazardous waste” S61 “Avoid release to the environment. Refer to special instructions/Safety data sheet”

### Justification for the proposal:

In acute toxicity tests with sodium hypochlorite in fish, *Daphnia magna* and algae, the lowest LC/EC50 values were 0.090, 0.005 and >0.06 mg/L (TRC). Sodium hypochlorite is not readily biodegradable. It is proposed, that on the basis of its acute toxicity sodium hypochlorite should be categorised as “Dangerous for the environment” (N), “Very toxic to aquatic organisms” (R50) and “May cause long-term adverse effects in the aquatic environment” (R53).

It is recommended that the active substance also carries the following ‘S’ safety phrases:

- S29 Do not empty into drains
- S56 Dispose of this material and its container to hazardous or special waste collection point
- S60 This material and its container must be disposed of as hazardous waste
- S61 Avoid release to the environment. Refer to special instructions/Safety data sheet

### **B.4.2 Proposals for the classification and labelling of preparations (Annex IIIA 12.3 and 12.4)**

See B.4.1.

The plant protection product is the same as the active substance (aqueous sodium hypochlorite solution containing 10 – 12% w/w available chlorine).

### **B.4.3 References relied on**

The proposed classification and labelling for the active substance is based on the evaluation as presented in section B.2, B.6 and B.9.

**B.5 Methods of analysis****B.5.1 Analytical methods for formulation analysis (Annex IIA 4.1; Annex IIIA 5.1)****B.5.1.1 Analytical methods for the determination of pure active substance in the active substance as manufactured (Annex IIA 4.1.1-4.1.2)**

From (RAR, 2007):

The sodium thiosulfate Method is typically used to determine the available chlorine. The solution is diluted, potassium iodine is added, and the solution is titrated with sodium thiosulphate.

In addition to the concentration hypochlorite, the pH and the density are important quality control parameters.

From (T.C.I., 2006, pamphlet 96):

Sodium can be determined with the EPA method 200.7: An Inductively Coupled Plasma - Atomic Emission Spectrophotometric method for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters, is described. Sodium is analyzed at a wavelength of 588.995 nanometers and has an estimated detection limit of 29 ug/l.

**B.5.1.2 Analytical methods for the determination of significant and/or relevant impurities and additives in the active substance as manufactured (Annex IIA 4.1.3-4.1.4)**

See confidential information (Volume 4, Annex C).

**B.5.1.3 Analytical methods for formulation analysis (Annex IIIA 5.1)**

See B 5.1.1.

**B.5.1.4 Analytical methods for the determination of breakdown products, isomers and additives**

See confidential information (Volume 4, Annex C).

### B.5.2 Analytical methods (residue) for plants, plant products, foodstuffs of plant and animal origin, feedingstuffs (Annex IIA 4.2.1; Annex IIIA 5.2)

The following residue definitions for monitoring are used for the assessment:

Food of plant origin	none
Food of animal origin	none
Soil	none
Water surface	sodium hypochlorite expressed as total available chlorine
drinking/ground	sodium hypochlorite expressed as total available chlorine
Air	none
Human tissues and body fluids	none

#### B.5.2.1 Enforcement methods

No methods in plant or animal products are required.

### B.5.3 Analytical methods (residue) soil, water, air (Annex IIA 4.2.2 to 4.2.4; Annex IIIA 5.2)

#### B.5.3.1 Residues in soil (Annex IIA 4.2.2)

No methods in soil are available. It is expected that sodium hypochlorite will react very soon with the organic matter and therefore will disappear rapidly.

#### B.5.3.2 Residues in water (Annex IIA 4.2.3)

From (RAR, 2007):

It is however important to know what the different methods are for determining available chlorine at low concentration in natural or wastewaters, fresh or seawater. Generally speaking, these methods were created in the USA or the UK for the analysis of drinking water.

The methods approved by the Standard Methods Committee in 1993 for fresh water use iodine, DPD (N,N-diethyl-p-phenylene-diamine) or syringaldazine. Amongst these three compounds, iodine is used for direct or indirect titration of chemicals and in potentiometric or amperometric methods. These four iodine methods can be used for natural or treated fresh or seawater. Only the iodometric back titration can be used for wastewater. The DPD methods are used for treated and waste freshwater using ferrous ammonium sulphate or by colorimetry. The syringaldazine colorimetric method has been developed specifically for free chlorine tests in treated fresh water. With colorimetric methods, organic contaminants may produce a false free chlorine reading, and sample colour and turbidity may interfere.

It is obvious that any test method should be used carefully. The method has to be appropriately chosen and adapted for each different matrix. It is particularly difficult to find an accurate method when the solution contains a lot of inorganic or organic compounds.

Hypochlorous acid in solution is particularly unstable. As shown in B2.1, exposure to sunlight or strong light will accelerate the transformation of hypochlorous acid into chloride. Agitation of the sample also accelerates this reduction process. Therefore, samples have to be analysed immediately after sampling, while avoiding light and agitation, and cannot be stored.

In the best conditions, the lowest accurate limit is 10 µg/l. In reality, in environmental aqueous media for ecotoxicology research, it would certainly be justifiable to restrict the lowest accurate limit to 100 µg/l for available chlorine.

All the research on sodium hypochlorite solutions in water highlights a particular problem of the analysis of the available chlorine remaining in the solution. Given the existence of three species of chlorine in the aqueous compartment (chlorine gas, hypochlorous acid, and hypochlorite anion) and their respective concentration depending on the pH, the total content of these three species has to be measured. This content of available chlorine does not include the concentration of combined chlorine (the heavy chloramines or the mono, di or trichlor- amines). For a very low content of available chlorine (0.2 mg/l), it is impossible to differentiate between free and combined chlorine. Many publications express the content as TRO which is a measure of total residual oxidant, including species like chloramines, bromine, chlorine dioxide.

ISO-method (ISO):

The ISO method 7393:1985 (part 1 to 3, part 1 corrected in 2001) are examples of methods using N,N-diethyl-p-phenylene-diamine or iodine for the determination of the concentration total free chlorine:

ISO method 7393-1:1985: specified for (amongst others) seawater; titration with N,N-diethyl-p-phenylene-diamine; LOQ 0.0004 mmol/L total Chlorine (~0.03 mg/L)

ISO method 7393-2:1985: specified for (amongst others) seawater; coulometric detection with N,N-diethyl-p-phenylene-diamine; LOQ 0.0004 mmol/L total Chlorine

ISO method 7393-3:1985: specified for water and drinking water; iodometric titration; LOQ 0.01 mmol/L total chlorine

ISO 7393-2 can be used for the determination of the amount of available chlorine and, with the used of potassium iodide, for the determination of the amount of total chlorine.

Several other methods are available for chlorine and/or sodium hypochlorite in water. Because there is an ISO method these are not mentioned.

### **B.5.3.3 Residues in Air (Annex IIA 4.2.4)**

No residue definition for air is proposed. However the following methods are available.

Only the determination of chlorine is regarded as meaningful. At pH between 3 and 9 the predominate form of sodium hypochlorite in water is HOCl and there is a small possibility that this will evaporate. The solubility in water HOCl is expected to be very high and evaporation is therefore expected to be very low.

For the determination of chlorine in air a validated NIOSH method, no 6011, is available (<http://www.cdc.gov/niosh/nmam/>). This method uses sampling on a silver filter and analysis with ionchromatography and a conductivity detector. The LOQ is 0.06 mg/m<sup>3</sup> Cl<sub>2</sub> (0.008 ppm).

In addition there are reaction monitoring tubes commercially available for workers to measure – semi-quantitative- the concentration of chlorine (and/or bromine) in air. With a change of colour the concentration of chlorine (and/or bromine) can be determined down to 0.2 ppm Cl<sub>2</sub> (1.5 mg/m<sup>3</sup>).

More information on monitoring can be found in the pamphlet 73 (T.C.I, 2003, pamphlet 73).

### **B.5.4 Analytical methods (residue) for body fluids and tissues (Annex IIA 4.2.5; Annex IIIA 5.2)**

Not required as sodium hypochlorite is not classified as (very) toxic.

### **B.5.5 Evaluation and assessment**

It is possible to determine the concentration of sodium hypochlorite in the technical material and formulation by measurement of the available chlorine content, in combination with the sodium content. Monitoring is not required in plant or animal products, nor in soil or in human body fluids or tissues. For water the ISO method 7393:1985 is available to determine the available chlorine concentration and for air (although not required) the NIOSH method, no 6011, is available to determine the concentration of chlorine.



**B.5.6 References relied on****References for the active substance**

Annex point/ reference no.	Author(s)	Year	Title Company, report no. Source (where different from company) GLP or GEP status (where relevant) Published or not	Data Protection Claimed Y/N	Owner
IIA 4.1	RAR (unknown)	2007	RISK ASSESSMENT REPORT FOR SODIUM HYPOCHLORITE, DRAFT  November 2007  Italy  non GLP  Published (via ECB website)	N	ECB
IIA 4.1.1; 4.1.2	T.C.I.	2006	Pamphlet 96, Sodium Hypochlorite Manual The Chlorine Institute inc. Edition 3, April 2006 Non GLP Published ( <a href="http://www.chlorineinstitute.org/">http://www.chlorineinstitute.org/</a> )	N	The Chlorine Institute
IIA 4.2.3	ISO	unkn won	ISO method 7393:1985- Water quality -- Determination of free chlorine and total chlorine  (part 1 to 3, part 1 corrected in 2001) available from <a href="http://www.iso.org">www.iso.org</a> published	N	ISO
IIA 4.2.4	T.C.I.	2003	Pamphlet 73, atmospheric monitoring equipment for chlorine The Chlorine Institute inc. Edition 7, June 2003 Non GLP Published ( <a href="http://www.chlorineinstitute.org/">http://www.chlorineinstitute.org/</a> )	N	The Chlorine Institute
IIA 4.2.4	Niosh	unkn won	Niosh method 6011 for the determination of chlorine in air ( <a href="http://www.cdc.gov/niosh/nmam/">www.cdc.gov/niosh/nmam/</a> ).	N	Niosh

**References for the plant protection product**

<b>Annex point/ reference no.</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title</b> <b>Company, report no.</b> <b>Source (where different from company)</b> <b>GLP or GEP status (where relevant)</b> <b>Published or not</b>	<b>Data Protection Claimed Y/N</b>	<b>Owner</b>
IIIA 5.1	RAR (unknown)	2007	RISK ASSESSMENT REPORT FOR SODIUM HYPOCHLORITE, DRAFT  November 2007  Italy  non GLP  Published (via ECB website)	N	ECB