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HEALTH RISK ASSESSMENT: GLOWSTICK (INGESTION AND DERMAL CONTACT)

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACRONYMS AND ABBREVIATIONS

ADI	Acceptable Daily Intake
ATBC	Tributyl acetyl citrate
BfR	The German Federal Institute for Risk Assessment
BPR	Biocidal Products Regulation
bw	Body weight
CAS RN	Chemical Abstracts Service Number
CDC	US Centers for Disease Control and Prevention
CGA	The Consumer Guarantee Act
CLP	Classification, Labelling and Packaging of Substances and Mixtures
CPPO	bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate
DBP	Dibutyl Phthalate
DEP	Diethyl Phthalate
DMP	Dimethyl Phthalate
ECHA	European Chemical Agency
EDTA	Ethylene diamine tetra acetic acid
EFSA	European Food Safety Authority
EPA	Environmental Protection Authority
ESR	Institute of Environmental Science and Research Limited
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
GPMT	Guinea Pig Maximisation Test
HSDIRT	Hazardous Substances Disease and Injury Reporting Tool
HSNO	Hazardous Substances and New Organisms
NOAEL	No-observed-adverse-effect level

NPC	New Zealand National Poisons Centre
NPDS	National Poison Data System (USA)
OECD	Organisation for Economic Co-operation and Development
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RfD	Reference dose
RIFM	The Research Institute for Fragrance Materials
SDS	Safety Data Sheet
TBC	Tributyl citrate
TCPO	bis(2,4,6-trichlorophenyl) oxalate
TDI	Tolerable Daily Intake
TEC	Triethyl citrate
TTC	Threshold of Toxicological Concern
WHO	World Health Organization

EXECUTIVE SUMMARY

The purpose of this report is to develop a generic health risk assessment for ingestion and dermal exposure to glow stick liquid contents This report will only consider domestic, non-occupational, routine and incidental exposure to the components of these products.

Glow sticks or light sticks are simple chemiluminescent systems, usually composed of an elongated flexible plastic tube containing two separated liquids. When the tube is deformed an inner (often glass) container ruptures, allowing mixing of chemicals and initiation of chemiluminescent reactions.

Glow sticks contain chemical substances such as hydrogen peroxide, dyes, alkyl citrates solvents (phthalates), and phenyl oxalate esters, e.g. CPPO. They are used for a variety of different reasons but are mainly recreational items found at night club settings, parties and festive gatherings. They are also used by the military and police with various operations.

Glow sticks are used seasonally during festivals (Halloween) or in events and parties. The exposure to glow stick liquid for consumers will only occur through improper treatment of the glow stick, resulting in the outer plastic tube being compromised. Such events would only be expected to occur once or a few times in a lifetime. Hence, chronic exposure is not expected. Children (up to 14 years age) are the most frequently exposed population by accidently chewing the glowstick and ingesting the liquid or splashing in the eyes or onto the skin. None of the chemicals used in the glow sticks are acutely toxic by oral and dermal routes.

Accidental and intentional incidents reported after exposure to liquid in glow sticks have generally resulted in asymptomatic or mild effects and no reports of serious adverse events or incidents requiring hospital admission were found. There were no cases of severe systemic toxicity reported. Following exposure, mild irritation was reported at the exposure site (eye, skin) which was transient. In very few incidents, nausea and vomiting was reported after ingestion of liquid. In most of the cases, remedial measures such as administration of fluids was recommended.

Overall, overseas surveillance data and case reports suggest that exposure to glow sticks or chemiluminescent products are unlikely to result in significant morbidity or mortality and any serious adverse events.

The toxicity of the constituent chemicals was summarised. These chemicals are generally of low acute toxicity and no acute health-based guidance values have been derived for any of the constituent chemicals. Consequently, no exposure estimates were derived in the current study.

1 INTRODUCTION

The purpose of this report is to develop a generic health risk assessment for ingestion and dermal exposure to the liquid contents of glow sticks, sometimes also known as light sticks. This report will only consider domestic, non-occupational, incidental exposure to hand glow stick contents. Exposure scenarios will be developed for the most common or likely exposure events.

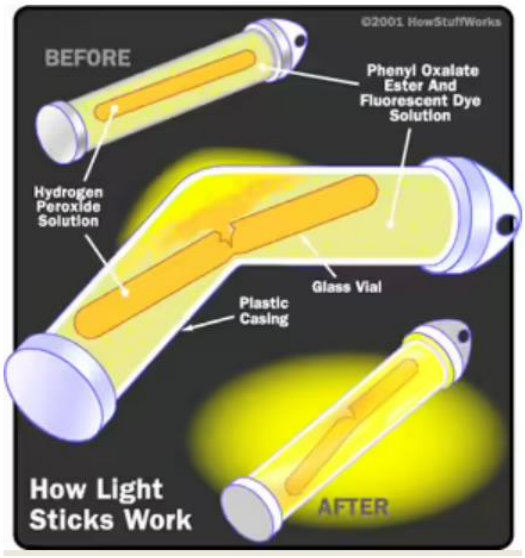
1.1 CONSUMER PRODUCTS DESCRIPTION – GLOW STICKS

Glow sticks or light sticks are simple chemiluminescent systems, usually composed of an elongated flexible plastic tube containing two separated liquids (BfR, 2009). When the tube is deformed an inner (often glass) container ruptures, allowing mixing of hydrogen peroxide (CAS RN) with an oxalic acid ester, such as bis(2,4,6-trichlorophenyl) oxalate (TCPO; CAS RN 1165-91-9) (Baldwin *et al.*, 2019).

Glow sticks may also contain solvents such as phthalates to dissolve chemicals, dyes, and to distribute the solution in the glow stick. Some of the phthalates used are dimethyl phthalate (CAS RN 131-11-3) and dibutyl phthalate (CAS RN 84-74-2) (Johnson Jr, 2002).

The reaction of the oxalate and hydrogen peroxide results in formation of a highly reactive dioxetanedione intermediate. The intermediate causes excitation of a fluorescent dye included in the glow stick liquid. As the dye relaxes to its ground state a photon of light is emitted. The wavelength of the photon and the resultant colour of the glow stick depends on the dye or mixture of dyes used (Baldwin *et al.*, 2019). The structure and principles of glow sticks are shown in Figure 1.

Figure 1. Structure and general principles of operation of glow sticks



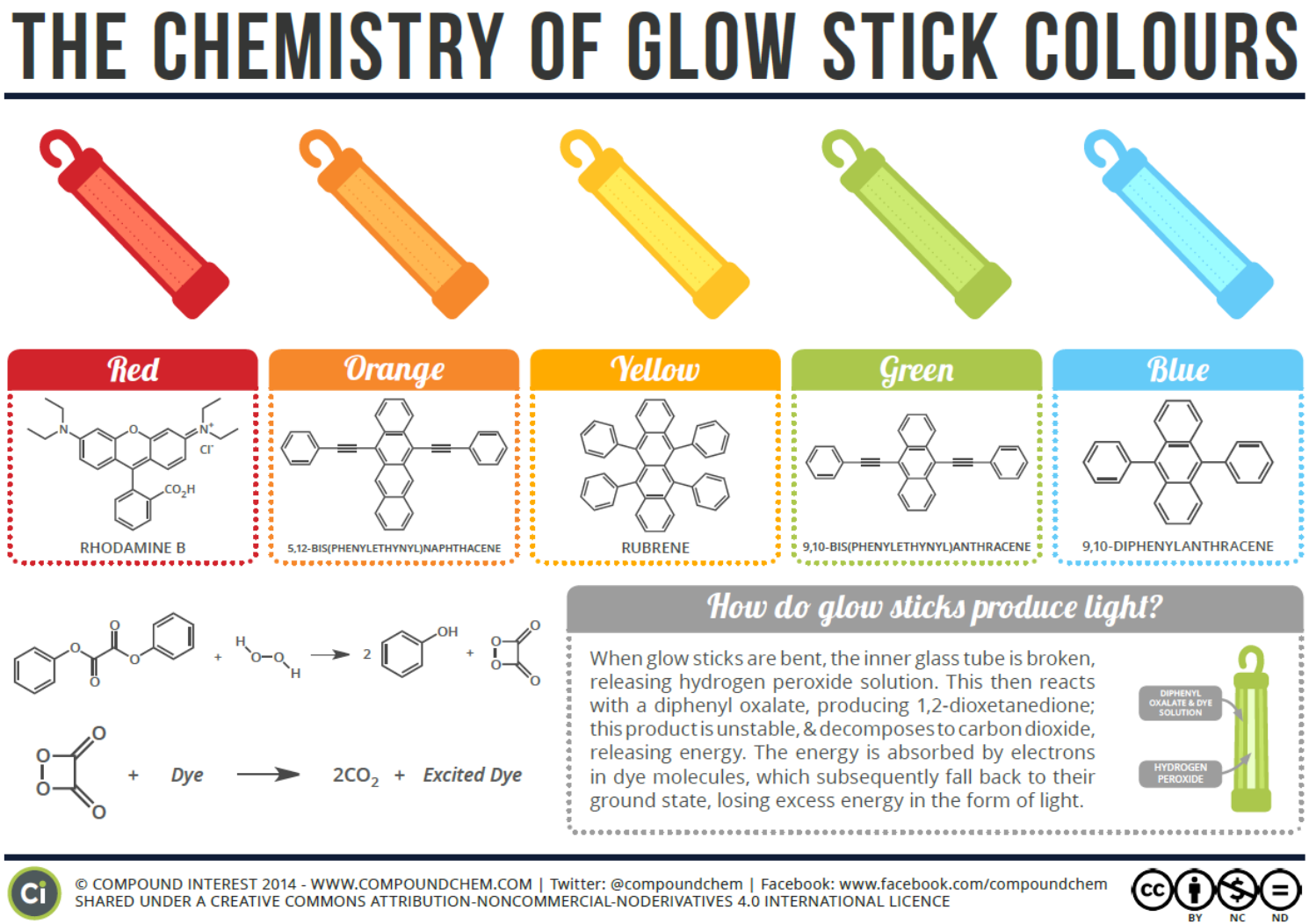
Glow sticks are used for a variety of different reasons but are mainly recreational items found at night club settings, parties and festive gatherings. They are also used by the military and police with various operations (Jacobsen *et al.*, 2013). Other uses include fishing, caving,

diving, camping, night golf, night sports, high visibility, table decorations, flower arranging and for fundraising and parties.

The principles, chemical reactions and dyes commonly used are shown in Figure 2.

The current assessment considered the available epidemiological evidence for adverse health effects due to exposure to glow stick liquids, but also considered the toxicology of the common components; TCPO and hydrogen peroxide and their reaction products and the commonly identified dyes shown in Figure 2.

Figure 2. Principles of glow stick chemiluminescence



1.1.1 CHEMICAL COMPOSITION OF GLOW STICKS

The Danish EPA carried out an assessment of glow sticks during 2012-2013 (Jacobsen *et al.*, 2013). The project included a survey and analysis of samples (n=15) of glow sticks which showed that 69 – 99% of the contents are composed of solvents. The analyses identified at least 70% of the chemical substances present (including the oxidising agent, H_2O_2) in glow sticks and in most cases identified more than 99% of the contents. Dyes were found to be present at very low concentrations; up to a maximum concentration of 0.1% (approx.). Other constituents included one or several phenyl oxalate esters, including bis(3,4,6-trichlor-2-carbopentoxyphenyl) oxalate (CPPO) at concentrations in the range 1-13.5%, other chemical substances (<10%), and various solvents (mainly phthalates or citrates). Compositional information for glow sticks is summarised in Table 1.

Table 1. Chemicals identities and typical concentrations of glow stick constituents

Chemical	CAS RN	Average concentration range
Butyl benzoate	136-60-7	4.1 – 24%
Dibutyl phthalate (DBP)	84-74-2	7.8 – 45%
Dimethyl phthalate (DMP)	31-11-3	30 – 87%
Tributyl acetyl citrate	77-90-7	0.4 – 25%
Tributyl citrate	77-94-1	40%
Triethyl citrate	77-93-0	40 – 55%
CPPO	30431-54-0	1 – 13.5%
Hydrogen peroxide	7722-84-1	0.4 – 2.4%
Various dyes	-	Up to 0.1%

Source: Jacobsen *et al.* (2013)
CPPO: bis(3,4,6-trichlor-2-carbopentoxy phenyl) oxalate

The total volume of liquid in the glow sticks sampled varied considerably from less than 100 µL in small glow sticks to 90 mL in the largest glow stick (Jacobsen *et al.*, 2013)

A wholesale supplier based in Palmerston North provided ESR with the safety data sheet (SDS) for one of their products (Trade name: glow liquid for glow stick- Blue). The supplier also confirmed that their products are not manufactured in New Zealand. The product is not classified as hazardous according to Regulation (EC) No 1272/2008 - classification, labelling and packaging of substances and mixtures (CLP) in the EU. The classification is based on the composition shown in Table 2.

Table 2. Chemical composition of a glow stick available in New Zealand

Chemical	CAS RN	Approximate concentration
Hydrogen peroxide	7722-84-1	1.75%
Tributyl acetyl citrate	77-90-7	43.86%
Triethyl citrate	77-93-0	48.25%
bis(2-carbopentyloxy-3,5,6-trichlorophenyl) oxalate	75203-51-9	6%
Dye [9,10-Bis(4-methoxyphenyl)-2-chloroanthracene]	110904-87-5	0.14%

1.2 REGULATION OF GLOW STICKS IN NEW ZEALAND

Glow sticks are manufactured articles and therefore are exempted under the Hazardous Substances and New Organisms Act 1996 (HSNO Act), administered by the Environmental Protection Authority (EPA). Although glow sticks contain hazardous substances, the product has an end use function wholly dependent on its shape and design, which does not involve the intentional release of any hazardous component (EPA, 2011).

The safety of glow sticks is under the general conditions of the Consumer Guarantees Act (CGA), 1993, which requires consumer products to be of acceptable quality, including safe to use.[1]

[1] https://www.legislation.govt.nz/act/public/1993/0091/latest/DLM311053.html Accessed 7 June 2022

2 HAZARD IDENTIFICATION

2.1 PREVIOUS ASSESSMENTS

No previous health impact assessments for glow sticks were found for New Zealand.

2.2 HEALTH EFFECTS – GLOW STICKS

2.2.1 Observations In humans

2.2.1.1 Incident surveillance - New Zealand

The National Poisons Centre (NPC) provided surveillance information on reported exposures to glow stick and glow bracelet materials (Lucy Shieffelbien, National Poisons Centres, personal communication). The NPC provided exposure records for the 12-year period from 1 January 2010 to 31 December 2021. A total of 1803 human exposures to glow stick/bracelet materials were identified, comprising 0.7% of all human exposure records. Overall, 63 (3.5%) of all 1803 exposures resulted in advice to seek medical assessment, while the remainder were advised on home care or that no treatment was necessary.

Children aged 1-5 and 6-10 years were most frequently reported as exposed to glow sticks and glow bracelets. For males and females combined, 1163 (64%) children aged 1-5 years and 416 (23%) children aged 6-10 years were reported as exposed to glow sticks/bracelets materials. Exposures were reported for all population age groups but for the age groups 11-15, 16-20 and over 20 years, no groups contributed more than 3% fo total exposures to glow stick/bracelet materials.

2.2.1.2 Incident surveillance – International

The Danish survey and health assessment of glow sticks (2013) reported information from the Poison Control Hotline at Bispebjerg Hospital, which had received 25 inquiries annually concerning glow sticks, often from young people who have bitten a hole in them. Injuries were rare, but sometimes stinging sensations in mouth and throat were observed (Jacobsen *et al.*, 2013).

A French report revealed 2979 cases of luminescent device exposure during the study period from January 1999 – December 2010. Data analysis indicated a rapid increase in incident cases over the decade covered, likely reflecting increased use of luminescent devices by the general population. Children aged 1 to 9 years were the most frequently exposed population (87% of total exposures). Ingestion of luminescent liquids was the most common route of exposure, with 85% of the 2979 cases categorised as oral exposure, 13% as eye exposure and 5% as skin exposure. Irrespective of the route of exposure, acute exposures were generally mild with moderate local irritation. There were no cases of severe systemic intoxication reported (DE TOXICOVIGILANCE, 2011).

A study in the US analysed data on paediatric and young adult exposures to chemiluminescent products reported to New York Poison Control Center between 1 January 2000 – 1 April 2001. There were 118 incidences of exposure which comprised 4 young adults (18 – 25 years), 18 teenaged children (13 – 17 years), and 96 younger children (0 – 12 years). Ingestion (92%) was the major route of exposure, followed by ocular (7.7%) and dermal (1%). Some adults (n = 4) were reported to accidentally swallow intact glow sticks during parties. Following exposure in patients who were exposed to chemiluminescent liquid from a leaking container, transient irritation at the exposure site was reported (23%). The patients who ingested intact glow sticks

did not experience aspiration or airway obstruction. There were no reported cases of systemic toxicity. Based on the data available, the authors concluded that “the reported exposure to chemiluminescent products is unlikely to result in significant morbidity or mortality” (Hoffman *et al.*, 2002).

A retrospective analysis of exposure events of light sticks/glow toys from the New South Wales Poisons Information Centre (NSWPIC) database, was performed on calls from 1 July 2013 to 30 June 2017. There were 2918 exposure events in total. Children aged 14 years and younger were most frequently exposed (94.1% of exposures). Ingestion (73%; a child chewing on a glow bracelet) was the major route of exposure followed by ocular (30.6%; a splash from a burst glow stick) and then dermal (6%). It should be noted that multiple exposure routes were reported in some instances (Cairns *et al.*, 2018). Characteristics of the exposure cases and exposure routes are included in Table 3.

Table 3. NSWPIC calls about glow sticks, by age and route of exposure, July 2013 to June 2017 (n = 2918)

Variable	Count	Proportion
Age group		
Infant (4 weeks-1 year)	24	< 1.0%
Toddler (1-4 years)	1617	55.4%
Child (5-14 years)	1105	37.9%
Adolescent (15-19 years)	23	< 1.0%
Adult (20-74 years)	124	4.3%
Unknown	22	< 1.0%
Route*		
Ingestion	2131	73.0%
Ocular	894	30.6%
Dermal	174	6.0%
Inhalation/nasal	25	< 1.0%
Buccal/sublingual	4	< 1.0%
Aural	2	< 1.0%

*One exposure may have more than one route of exposure coded, so percentages add up to more than 100%

Acute exposures to glow sticks are relatively benign and there was no mortality or morbidity reported in the cases summarised in this study. Most callers (91.3%) were advised to stay home, with only 15 (including 13 ocular exposures) referred to hospital, reflecting the low toxicity of these products. The first aid for glow stick exposures is simple, and they very rarely require any medical attention (Cairns *et al.*, 2018).

Since 2005, the Berlin Poison Information Centre have recorded a major increase in accidents involving glow sticks. Adolescents as well as their younger siblings were most commonly affected. A total of 105 enquiries were recorded in 2005, which increased to 393 in the year 2008 (Meyer *et al.*, 2009). In reporting to the *Bundesinstitut für Risikobewertung* (BfR) only single cases were reported in each of 1998, 2007 and 2008, but by late 2009, 31 cases of accidental ingestion had been reported, with 28 cases of ingestion recorded within a span of 10 days. Health impairment was minor in 8 cases and in one case the severity could not be assessed. No symptoms occurred in all other cases. Eye irritation, vomiting, or nausea were reported by two patients each. In one case, disturbance of consciousness was observed and dermal/mucosal swelling in another. Most cases were reported in young children (n = 20), some school children (n= 9) and two adults. Ingestion was the major route of exposure (n = 30) followed by ocular (n = 3) and dermal (n = 1) (Meyer *et al.*, 2009).

2.2.1.3 Case reports

Very limited case reports were found in the literature due to glow sticks exposure to humans. Children were found to be the most exposed population to glow sticks. There were 3 cases published in the BfR report “Cases of Poisoning Reported by Physician”. Additionally, one exposure event in an adult male was reported in BroBible (non-scientific source, lifestyle publisher).

In a case report published by BfR, a 2-year-old boy chewed a glow stick which then cracked and as a result, the boy ingested a small amount of leaking liquid. He was taken to a paediatric hospital by his parents and was drowsy at admission. However, this was not attributed to the

ingestion of glow stick liquid, but rather due to the late time (9:00 pm) of the incident. There were no pathological findings on physical examination. A poison centre was contacted by the hospital which did not recommend any further treatment or measures (Meyer *et al.*, 2009).

A 7-year-old girl chewed a glowstick on Halloween evening. The glow stick cracked which resulted in ingestion of a small amount of liquid. The girl experienced an episode of vomiting which came to an end while the parents were contacting the poison centre for advice. The girl developed a characteristic irritation of the gastrointestinal tract. The parents were recommended to administer fluids as the only remedial measure. There was no need to see a doctor (Meyer *et al.*, 2009).

A 5-year-old boy chewed a glowstick on Halloween evening. The glow stick cracked which resulted in ingestion of a small amount of the liquid leaking from it. In addition, he also rubbed some of the liquid into his eye producing reddening and a burning sensation in the eye. He was taken to a hospital by his parents. The eye was still reddened and the burning sensation continued while in the hospital. There were no pathological findings on physical examination and he was administered fluids by oral route as the sole treatment (Meyer *et al.*, 2009).

An article published on a lifestyle website (brobible) reported that a man ingested the contents of six glow sticks because the package told him not to. There was a burning sensation in his mouth and throat, but he kept drinking the liquid. The pain grew intense within hours, and he had to call emergency services. In the emergency room, he displayed symptoms of nausea and insomnia (Anderson, 2021).

2.3 TOXICITY OF GLOW STICKS

No toxicity studies on formulated glow stick liquid were found in the literature. Hence, the toxicity was evaluated based on individual chemical components. As discussed in the introduction of this document, glow sticks generally contain solvents (DMP, DBP), hydrogen peroxide, an oxalic acid ester, such as TCPO, and a dye.

It is likely that human exposure to glow stick liquid would only occur once or a few times in a lifetime. Hence, acute toxicity endpoints (oral, dermal, inhalation), skin/eye irritation and skin sensitisation are discussed for the chemical components. Chronic toxicity endpoints (long term toxicity (90-day, 1-year), carcinogenicity, and reproductive toxicity) are not discussed.

There was no acute toxicity data available in the literature for dyes and oxalic acid esters such as TCPO.

2.3.1 Hydrogen peroxide (CAS RN 7722-84-1)

Hydrogen peroxide is a highly reactive, strongly oxidising agent and degrades (through reaction) rapidly in contact with organic material. When it comes into contact with skin it rapidly reacts and has local effects rather than systemic (CIR, 2018).

The acute toxicity of hydrogen peroxide is concentration and dose dependent. It is moderately toxic by oral and inhalation routes. However, it has low dermal toxicity (NICNAS., 2014). Clinical signs of toxicity after oral exposure in rats administered 35% aqueous hydrogen peroxide or greater concentrations included tremors, decreased motility, prostration, and oral, ocular, and nasal discharge. Most rats that died had reddened lungs, haemorrhagic and white stomachs, and blood-filled intestines; some had white tongues (CIR, 2018). The LD_{50} (oral & dermal) values reported in the literature are given below (Table 4).

Table 4. Acute lethal dose (LD_{50}) of hydrogen peroxide

Species	Concentration	LD_{50} (mg/kg)
Oral		
Rat	10%	1520- >5000
Rat	35%	1193 (m)
		1270 (f)
Rat	60%	872 (m)
		801 (f)
Rat	70%	75 - 1026
Mice	90%	2000
Dermal		
Rabbit	90%	700 - 5000
	70%	9200
	35%	2000

Source: (CIR, 2018; JRC, 2003; NICNAS, 2014)

The irritation and corrosivity of hydrogen peroxide to skin and eyes is also concentration dependent. In rabbits, H_2O_2 solutions of 10% were slightly irritating to the skin, 35% solutions proved to be moderately irritating and caused delayed epidermal necrosis and sloughing, while 50% solutions and more concentrated solutions were severely irritating and corrosive (HERA, 2005). In humans, H_2O_2 has been reported to cause transient (lasting 10 to 15 min after 1 min exposure) dermal blanching at concentrations of 3% or greater (CIR, 2018). Hydrogen peroxide (70% aqueous) is corrosive to the rabbit eye. H_2O_2 (8, 10 and 15%) was severely irritating to the eyes of rabbits whereas 5% H_2O_2 caused mild eye irritation (JRC, 2003; NICNAS, 2014). In human eyes, 1 to 3% aqueous H_2O_2 causes severe pain which rapidly subsides. However, hydrogen peroxide has been historically used at these concentrations as an ocular antibacterial agent, as much as three to five times per day, without significant injury. While the threshold for eye irritation in many subjects is considered to be 100 ppm (0.01% aqueous), even at 800 ppm (0.08% aq.), hydrogen peroxide has been shown to not cause corneal or conjunctival epithelial staining; higher levels may result in greater discomfort (CIR, 2018).

2.3.2 Dimethyl phthalate (DMP; CAS RN 131-11-3)

DMP is of relatively low acute toxicity by oral and dermal exposure routes. The oral and dermal LD_{50} is >2000 mg/kg bw in rats and rabbits (NICNAS, 2014a). A study, included in the REACH dossier, reported oral and dermal LD_{50} (rat) values of 8500 and >12000 mg/kg bw, respectively. Signs of intoxication in the rat included drowsiness within the first 15 min after an acute oral dose. Animals rapidly became semi-conscious, deaths occurred between 7 h and 3 days (ECHA, 2022b).

DMP is slightly irritating to eyes and skin in animals and humans. The effects observed do not meet the threshold to be classified as a skin/eye irritant in GHS v7.0 (ECHA, 2022c; NICNAS, 2014a).

2.3.3 Dibutyl phthalate (DBP; CAS RN 84-74-2)

DBP has low acute toxicity by oral, dermal and inhalation routes. The LD_{50} for oral and dermal routes are ≥6,300 (rats) and >20,000 (rabbits) mg/kg bw, respectively. The 4 hour LC_{50} in rats

was ≥ 15.68 mg/L. A reduction in respiratory rate was observed at 15.68 mg/L. Excessive grooming in surviving animals led to persistent poor coat condition throughout the study. Macroscopy of the lungs revealed white foci in all lobes in one male and one female rat at 15.68 mg/L, and dark red regions in two female rats at 12.45 mg/L, and one male and one female rat at 16.27 mg/L (JRC, 2004).

DBP was found to be a very mild skin and eye irritant in rabbits. No signs of sensitisation were observed in two guinea pig maximisation tests (GPMT) (JRC, 2004).

DBP is identified as a substance of very high concern (SVHC) in accordance with the REACH regulation in the EU. DBP has been shown to adversely affect the endocrine system of mammals primarily through *in vivo* findings on reduced foetal testosterone. These findings are further substantiated by mechanistic findings, also *in vivo*, of downregulation of genes in the steroidogenic biosynthesis pathway. The spectrum of adverse effects observed in rats include increased nipple retention, decreased anogenital distance, genital malformations, reduced number of spermatocytes and testicular changes including multinucleated gonocytes, tubular atrophy and Leydig cell hyperplasia.
Based on these effects, DBP is classified as reproductive toxicity category 1 (May damage fertility or the unborn child) in New Zealand by EPA and reproductive toxicity category 1B (May damage the unborn child. Suspected of damaging fertility) in the EU by ECHA (ECHA, 2022g; EPA, 2022).

2.3.4 Tributyl acetyl citrate (ATBC, CAS RN 77-90-7)

ATBC has low acute toxicity by oral route in rats and mice. In rats, no mortality and significant signs of toxicity were observed at doses in the range 10,500-31,500 mg/kg. The LD_{50} was >31,500 mg/kg. In cats, the LD_{50} was >52,500 mg/kg. Mortality was not observed (ANSES, 2016b; Johnson Jr, 2002). Signs of toxicity included slight nausea and diarrhoea, which subsided in less than 24 hours following dosing. In acute dermal toxicity studies in guinea pigs, no signs of toxicity were observed up to dose levels of 10,250 mg/kg (ANSES, 2016b).

There were no data on acute inhalation toxicity. ATBC is anticipated to have very low potential for inhalation toxicity due to its low vapour pressure and high oral LD_{50}.

ATBC is not a skin irritant or skin sensitiser, based on animal and human studies. In a repeated insult patch test in 50 volunteers (men and women from 21 to 60 years), occlusive patches (one per test substance) moistened with 0.4 mL of the ATBC solution were applied to the upper arms of each subject for 3 consecutive weeks. Duplicate challenge applications of each test material were made after a 2-week non-treatment period. Challenge reactions were scored at 48 and 96 hours post application. There was no evidence of irritation, nor any reactions suggestive of contact sensitisation in subsequent challenge tests (ANSES, 2016b). ATBC was not a skin irritant in rabbits at a concentration of 1000 mg/kg (CIR, 2019). ATBC (0.05-1%) induced pale, pink erythema with oedema in three guinea pigs and faint, pink erythema with oedema in one guinea pig. It was not classified as a skin irritant. ATBC (50%) did not cause skin sensitisation in the guinea pig maximization test (GMPT) (ANSES, 2016b; Johnson Jr, 2002).

ATBC was a mild eye irritant in rabbits and caused moderate erythema in one rabbit within 20 minutes. No irritation was observed at 48 or 72 hours post instillation. The effects observed do not meet the threshold to be classified as an eye irritant in GHS v7.0 (ANSES, 2016b).

2.3.5 Tributyl citrate (TBC, CAS RN 77-94-1)

TBC has low acute toxicity by the oral route in rats. In rats, no mortality and significant signs of toxicity were observed at doses in the range 10,800-32,400 mg/kg. The LD_{50} was >31,500 mg/kg (USCPSC, 2019). There was no acute toxicity (dermal, inhalation), skin/eye irritation data available in the literature. ATBC and TBC metabolise to a common compound, but the study reporting this outcome was very limited and had no toxicokinetic information on TBC. Therefore, a read across assessment using ATBC is not currently feasible.

Read across is also not supported for irritation and sensitisation as TBC may be more reactive than ATBC at the site of contact (ANSES, 2016a).

2.3.6 Triethyl citrate (TEC, CAS RN 77-93-0)

TEC is not acutely toxic by the oral route. The LD_{50} value in rats is 7 g/kg. It was found to be a strong sensitiser in guinea pigs. However, it did not induce sensitisation and skin irritation in humans following repeated insult patch test (EC, 1999). No other toxicological data on TEC was found in the literature.

2.3.7 Butyl benzoate (CAS RN 136-60-7)

Butyl benzoate is of relatively low acute toxicity by oral, dermal and inhalation exposure routes. In well conducted toxicity studies, following OECD test guidelines, the LD_{50} was >2000 mg/kg by oral and dermal route in rats. No abnormal clinical signs were observed during the acute oral toxicity study. After 24-hr dermal exposure, abnormal gait and stance was observed immediately after exposure. No erythema or oedema were observed at the application sites during the study.

Butyl benzoate is slightly irritating to eyes and skin in rabbits. However, the effects observed do not meet the threshold to be classified as a skin/eye irritant in GHS v7.0 (ECHA, 2022f).

3 DOSE-RESPONSE INFORMATION

No dose-response information specific to glow sticks or light sticks was found. There were no acute health-based guidance values reported for the chemicals in the glow stick.

3.1 HYDROGEN PEROXIDE (CAS RN 7722-84-1)

In a 90-day inhalation toxicity study rats (10/sex/group), received hydrogen peroxide (50% w/w) at the concentrations of 0, 1.02, 2.51, 7.08 ppm (0, 1.5, 3.6, 10.3 mg/m^3) for 6 hours per day and 5 days per week. There were no treatment related effects on body weight or food consumption. There was a statistically significant increase in alkaline phosphatase concentrations in male animals at 10 mg/m^3 which was within the range of the historical control data and was not considered adverse. In addition, liver and thymus weights (both absolute and relative to body weight) of male animals at 10 mg/m^3 were statistically significantly decreased. However, this weight change was not accompanied by microscopic abnormalities in these organs and values were consistent with historical control data. In the absence of any significant and relevant adverse effects, a NOAEC of 10 mg/m^3 was proposed for male and female animals (ECHA, 2022d). An uncertainty factor of 8 was applied to derive an external reference value (AEC) of 1.25 mg/m^3. This value was extrapolated to acute, medium and long-term exposure durations.

Study (key effect)	POD	Uncertainty factors	Reference dose	Reference
90-day inhalation toxicity rat study (NOAEC is the highest dose)	NOAEC: 10 mg/m^3	8	AEC inhalation (acute, medium, long-term): 1.25 mg/m^3	(ECHA, 2015)

It should be noted that the NOAEC is the highest concentration in the study. Hence, it is uncertain at what dose systemic effects would occur.

3.2 BUTYL BENZOATE (CAS RN 136-60-7)

There were no health-based guidance values available for butyl benzoate in the literature due to insufficient repeated dose toxicity data. In a safety assessment carried out by the Research Institute for Fragrance Materials (RIFM), the total systemic exposure to butyl benzoate (0.002 µg/kg/day) was below the threshold of toxicological concern (TTC) (30 µg/kg bw/day; Kroes et al., 2007) for the repeated dose toxicity endpoint of a Cramer Class I[2] material at the current level of use (Api *et al.*, 2018).

3.3 DIMETHYL PHTHALATE (DMP; CAS RN 131-11-3)

There were no health-based guidance values available for DMP in the literature. However, the physical-chemical (MW, LogP etc), metabolic pathways and toxicological properties are similar to diethyl phthalate. Hence, the oral reference dose (RfD) proposed by US EPA for DEP can be used for DMP. However, this RfD is not applicable to acute exposure situations.

[2] The Cramer classification system assigns chemicals to one of three toxicity classes based on structural features.

Study (key effect)	POD	Uncertainty factors	Reference dose	Reference
Sub chronic oral (dietary) toxicity study; rats (Decreased growth rate, food consumption and altered organ weights)	NOAEL: 750 mg/kg bw/d	1000	Oral RfD: 0.8 mg/kg bw/d	(IRIS, 1987)

3.4 DIBUTYL PHTHALATE (DBP; CAS RN 84-74-2)

US EPA has reported a chronic oral RfD for DBP based on the mortality observed at the highest dose (600 mg/kg/day) in a 1-year rat study. One-half of all rats receiving this dose died during the first week of exposure. The remaining animals survived with no apparent ill effects. There was no effect of treatment on gross pathology or haematology. The NOAEL was determined to be 125 mg/kg/day. The overall confidence in the RfD was low as the study used few animals and of one sex only. While it was stated that several organs were sectioned and stained, no histopathologic evaluation was reported (IRIS, 1987a).

The EFSA Panel on Food Contact Materials, Enzymes and Processing Aids (CEP Panel) set tolerable daily intakes (TDIs) for five phthalates on a temporary (t-) basis. The group included DBP. The grouping was based on structural similarity, similar use and exposure pattern, similar toxicokinetics, similar reproductive toxicity related to anti-androgenic effects, inhibition of the testosterone production in foetal rats and changes in germ cell differentiation. Hence, a group t-TDI for the phthalates of 0.05 mg/kg bw per day expressed as DEHP equivalents was set (EFSA Panel on Food Contact Materials *et al.*, 2019).

Kortenkamp and Koch (2020) suggested new reference doses for phthalates used in mixture risk assessment. A RfD of 6.7 µ/kg bw/d was derived for DMP based on a LOAEL of 2 mg/kg bw/d from a developmental toxicity study in rats. In this study maternal rats were given DBP at dietary concentrations of 0, 20, 200, 2000 and 10,000 ppm from gestational day 15 to postnatal day (PND) 21. From 20 ppm, reduction of testicular spermatocyte development was observed at PND21 and mammary gland changes at low incidence in both sexes. Male offspring showed a decreased neonatal anogenital distance and retention of nipples (PND 14) at the highest dose while females showed a slight non-significant delay in the onset of puberty. A NOAEL for DBP could not be established in this study while a LOAEL of 20 ppm (1.5 – 3 mg/kg bw/d) was determined in the maternal diet (Lee *et al.*, 2004).

Study (key effect)	POD	Uncertainty factors	Reference dose	Reference
1-year oral (dietary) toxicity study; rats (m) (increased mortality)	NOAEL: 125 mg/kg bw/d	1000	Oral RfD: 0.125 mg/kg bw/d	(IRIS, 1987a)
Three-generation reproductive toxicity study in rats (effects on	NOAEL: 4.5 mg/kg bw/d	100	TDI: 0.05 mg/kg bw/d (expressed as DEHP equivalents	(EFSA Panel on Food Contact Materials *et al.*, 2019)

the testis in F1 animals)				
Developmental toxicity study (reduction of testicular spermatocyte developmen)	LOAEL: 2 mg/kg bw/d	100 x 3	Oral RfD: 0.0067 mg/kg bw/d	(Kortenkamp and Koch, 2020; Lee *et al.*, 2004)

3.5 TRIETHYL CITRATE (CAS RN 77-94-1)

JECFA reported an ADI of 20 mg/kg bw for triethyl citrate based on a NOAEL (top dose level) of 2000 mg/kg bw per day from a two-year feeding study in rats. Weight gain and food intake were reduced below that of the control groups when the level of the compound in the diet was increased. (No specific numbers were given for these results.) No adverse effects on haematology, urinalysis, survival, gross or histopathologic parameters could be attributed to triethyl citrate.

Study (key effect)	**POD**	**Uncertainty factors**	**Reference dose**	**Reference**
2-year oral (dietary) toxicity study; rats (m) (increased mortality)	NOAEL: 2000 mg/kg bw/d	100	ADI: 20 mg/kg bw per day	(JECFA, 1999)

3.6 TRIBUTYL ACETYL CITRATE (ATBC, CAS RN 77-90-7)

EFSA established a tolerable daily intake (TDI) of 1 mg/kg bw per day (EFSA, 2005a) by applying the default uncertainty factor of 100 to the NOAEL of 100 mg/kg bw/day for general toxicity derived from oral toxicity studies in rats (Harmon and Otter, 2022).

3.7 TRIBUTYL CITRATE (TBC, CAS RN 77-94-1)

There were no health-based guidance values available for tributyl citrate due to extremely limited toxicological database.

3.8 SUMMARY

Health-based guidance values (HBGVs), based on a point of departure of the dose-response relationship, have been established for some, but not all, of the chemicals commonly included in glow stick liquid. However, these HBGVs have only been derived for assessment of chronic exposure, with the exception of the AEC derived for hydrogen peroxide, which is applicable to acute exposure by inhalation. The chemicals used in the glow sticks have a very low acute toxicity potential by oral, dermal and inhalation exposure.

4 EXPOSURE ASSESSMENT

The consumer exposure to glowsticks is qualitatively assessed as there are no acute health-based guidance values for the chemical components.

The incidents reported in the literature as well as cases in New Zealand show that the consumers are likely to be exposed to the chemicals through dermal, oral and ocular routes. Exposure via the inhalation route is very unlikely due to the physico-chemical properties of the chemicals and due to the use patterns of the products (Jacobsen *et al.*, 2013).

4.1 DERMAL EXPOSURE

Exposure to skin can occur while snapping the glow stick when the outer material breaks and the liquid splashes onto the skin. This is most likely to be unintentional or accidental. It is assumed that the exposure can occur to the whole liquid in a glow stick (up to 90 mL). Exposure is likely to be of short duration, except in instances where clothing becomes impregnated with the liquid and the clothing is not removed.

4.2 ORAL EXPOSURE

Oral exposure can occur due to intentional or unintentional ingestion of the liquid from the product. This can happen after snapping the product and while the product is luminous the outer material might break due to unintentional and inappropriate use, e.g., by biting or hitting against a sharp object. It is reasonable to assume the worst-case scenario that the entire contents (up to 90 mL) could be swallowed in this situation. However, the liquid is unlikely to taste pleasant and, in most cases, exposure will be to substantially less than 90 mL.

4.3 OCULAR EXPOSURE

Eye exposure can occur while snapping the glow stick when the outer material breaks and the liquid splashes in the eyes. This can also happen if the glow stick is carried on the head or face (caps and glasses). Eye exposure may also occur secondarily to slipping the liquid onto the skin of the hands, through rubbing of the eyes. As this kind of exposure will likely be accidental, it is reasonable to assume that maximum exposure to a constituent will be a sub-amount of the total volume of the glow stick.

5 RISK CHARACTERISATION

The inconsistent and sometimes conflicting nature of dose-response information for the chemicals in glow sticks makes definitive characterisation of risks problematic. The chemicals have generally been reported to be of low acute toxicity and no acute HBGVs are available for oral or dermal exposure. The following sections provide largely qualitative assessments of the likely risks from ingestion and dermal exposure of chemicals in the glow stick.

5.1 HYDROGEN PEROXIDE

The toxicity of hydrogen peroxide is concentration dependent. It is unlikely that it will cause any acute systemic toxicity by the oral, dermal and inhalation route.

As discussed in section 2, the skin/eye irritancy is also concentration dependent. Based on the available data, ECHA has established specific concentration limits (SCL) for hydrogen peroxide. SCL are limits assigned to a substance indicating a threshold at or above which the presence of that substance in a mixture leads to the classification of a mixture as hazardous. The SCLs for hydrogen peroxide in the EU are (ECHA, 2015):

Eye Damage 1; H318 (Causes serious eye damage): 8 % ≤ C < 50%
Eye Irritation 2; H319 (Causes serious eye irritation): 5 % ≤ C < 8%
Skin Corrosion 1A (Causes severe skin burns and eye damage); H314: C ≥ 70 %
Skin Corrosion 1B (Causes severe skin burns and eye damage); H314: 50 % ≤ C < 70%
Skin Irritation 2; H315 (Causes serious eye irritation): 35 % ≤ C < 50%

As per the analytical results published in the survey done by Danish EPA, the maximum concentration of hydrogen peroxide in glow sticks was 2.4% (Jacobsen *et al.*, 2013). At this concentration, none of the above hazard classification criteria would be triggered and therefore it is unlikely that hydrogen peroxide will cause any serious eye/skin irritation or corrosion. However, it may cause mild skin/eye irritation which can be treated by washing eyes with water.

5.2 PHTHALATES

There were two phthalates (DBP and DMP) found in the chemical analysis of glow sticks in Denmark. The average concentrations of DBP and DMP were in the rage of 7.8 – 45% and 30 – 87%, respectively (Jacobsen *et al.*, 2013). The SDS provided by one of the sellers in New Zealand showed the glow liquid for glow stick did not contain any phthalates. However, the presence of phthalates in glowstick products in New Zealand cannot be excluded based on the SDS provided.

Both phthalates found in glow sticks are of low acute toxicity by oral and dermal route. They are mild skin and eye irritants, which can be treated by washing eyes with water. DBP is classified as reproductive toxicity category 1 (May damage fertility or the unborn child) in New Zealand by the EPA and reproductive toxicity category 1B (May damage the unborn child. Suspected of damaging fertility) in the EU by the ECHA (ECHA, 2022g; EPA, 2022). Although DBP is a reproductive and developmental toxicant and a SVHC, it is not clear if this toxicological property extends to single exposure scenarios and specific data are not available to evaluate this possibility. For the purpose of the current report, it has been assumed that a repeated exposure to DBP would be required for any reproductive or developmental toxicity to occur.

5.3 ALKYL CITRATES

There were three alkyl citrates (TBC, TEC and ATBC) found in the chemical analysis of glow sticks in Denmark. TBC, TEC and ATBC are, or are expected to be, of low acute toxicity by oral and dermal routes. None of the citrates is known to cause serious skin or eye irritation. However, they may cause mild skin/eye irritation which can be treated by washing with water.

5.4 BUTYL BENZOATE

Butyl benzoate is expected to be of low acute toxicity by oral and dermal route. It does not cause serious skin or eye irritation. However, it may cause mild skin/eye irritation which can be treated by washing with water.

6 CONCLUSIONS

Glow sticks or light sticks are simple chemiluminescent systems, usually composed of an elongated flexible plastic tube containing two separated liquids. Glow sticks contain chemical substances such as hydrogen peroxide, dyes, solvents (alkyl citrates and/or phthalates), and phenyl oxalate esters, e.g. CPPO. The total volume of liquid in the glow stick has been reported to vary from less than 100 µL in small glow sticks to 90 mL in the largest glow stick. Glow sticks are used for a variety of different reasons but are mainly recreational items found at night club settings, parties and festive gatherings. They are also used by the military and police with various operations.

Glow sticks are used seasonally during festivals (Halloween) or in events and parties. The exposure to glow stick liquid for consumers will only occur through improper treatment of the glow stick, resulting in the outer plastic tube being compromised. Such events would only be expected to occur once or a few times in a lifetime. Hence, chronic exposure is not expected. Children (up to 14 years age) are the most frequently exposed population by accidently chewing the glowstick and ingesting the liquid or splashing in the eyes or onto the skin. None of the chemicals used in the glow sticks are acutely toxic by oral and dermal routes. Although DBP is a reproductive and developmental toxicant and a SVHC, it is not clear if this toxicological property extends to single exposure scenarios and specific data are not available to evaluate this possibility. For the purpose of the current report, it has been assumed that a repeated exposure to DBP would be required for any reproductive or developmental toxicity to occur.

Accidental and intentional incidents reported after exposure to liquid in glow sticks have generally resulted in asymptomatic or mild effects and no reports of serious adverse events or incidents requiring hospital admission were found. There were no cases of severe systemic toxicity reported. Following exposure, mild irritation was reported at the exposure site (eye, skin) which was transient. In very few incidents, nausea and vomiting was reported after ingestion of liquid. In most of the cases, remedial measures such as administration of fluids was recommended.

Overall, overseas surveillance data and case reports suggest that exposure to glow sticks or chemiluminescent products are unlikely to result in significant morbidity or mortality and any serious adverse events.

The toxicity of the constituent chemicals was summarised. These chemicals are generally of low acute toxicity and no acute health-based guidance values have been derived for any of the constituent chemicals. Consequently, no exposure estimates were derived in the current study.

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