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Survey and health assessment of glow sticks

Survey of chemical substances in consumer products No. 122, 2013

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Survey and health assessment of glow sticks

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Contents

Foreword

The project ”Survey and health assessment of glow sticks” was carried out from July 2012 till May 2013.

This report describes the project results, including a survey, chemical analyses of selected substances in the glow stick liquids and an assessment of the exposure and health hazards to consumers.

The project was carried out by Danish Technological Institute. Participants from Danish Technological Institute were Eva Jacobsen (project manager), Kathe Tønning, Lone F. Poulsen, Grith Kastorp and Niels Elmegaard.

The progress, development and results of the project were assessed by a steering group consisting of the following persons:

Shima Dobel, the Danish Environmental Protection Agency
Lærke Ambo Nielsen, the Danish Environmental Protection Agency
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Niels Elmegaard, Danish Technological Institute

The project was financed by the Danish Environmental Protection Agency.

Conclusion and Summary

Glow sticks are disposable and consist of a plastic tube or other container with two chemical solutions that create a fluorescent colour when they are mixed.

This project has investigated glow sticks that appeal to children either because they can be used as toys, as articles for gimmicks and gags or as personal ornamentation/jewellery.

Legislation
Glow sticks fall within the European Community Regulation on chemicals called REACH. According to REACH, glow sticks belong to the product group that is a combination of an article and ”a chemical mixture in a tube”. If the product is sold to private consumers, it must not contain CMR substances (carcinogenic, mutagenic or toxic for reproduction) in concentrations that would result in the product having to be classified as carcinogenic, mutagenic or toxic for reproduction. If the product is used for personal ornamentation, gimmicks and gags or the like, then the product must not contain fluid dangerous substances or mixtures in concentrations that would lead to the product having to be classified as hazardous.

Chemical mixtures are comprised by the regulation on classification, labelling and packaging of dangerous substances and mixtures (CLP Regulation). Materials containing mixtures with concentrations assessed to be dangerous to health or the environment have to be classified and labelled according to the regulation.

According to the Executive Order for Toys, toys for children up to the age of 3 must not contain dangerous substances or preparations that can be hazardous to the health of the children who use them. Special rules apply to certain phthalates in toys.

Assessment of exposure
The most common exposure is assessed to be skin contact, swallowing or splashes in eyes. Exposure is expected to only take place once or a few times in a lifetime.

No Danish statistics exist on exposure to glow sticks or treatment after accidents with glow sticks, but the Poison Control Hotline at Bispebjerg Hospital has informed that they receive app. 25 inquiries annually concerning glow sticks; often from young people who have bitten a hole in them. Injuries are seldom, but now and then stinging sensations in mouth and throat are seen. Asthma-Allergy Denmark and the Information Centre on Environment and Health state that they have not registered inquiries regarding glow sticks.

Results of the survey
The survey only comprised glow stick products that are marketed in Denmark or that are sold on Danish/ Danish-language internet pages and that are intended for children or that appeal to children. Therefore, they can be toys as well as articles for gimmicks and gags. Children are defined as children under the age of 14. The survey was carried out in the period from June-August 2012.

When visiting a number of retail shops and internet shops, glow sticks were registered in a number of different colours and the most common are blue, red, yellow, green, pink and orange. Glow sticks mainly exist as seasonal goods in the shops' product ranges, e.g. in connection with Halloween and New Year's Eve. Mainly glow sticks or rods with connectors for making bracelets or necklaces are in question. Glow sticks are also available as part of a larger assembly kit with which you make your own e.g. ”earrings”, ”glasses” and ”caps” with the enclosed sticks, connectors and other parts.

Inquiries to manufacturers/importers/distributors showed that a limited number of glow stick manufacturers exist and to a great degree the same products can be purchased e.g. in online stores. Response was received with information about contents from six different manufacturers.

Results of chemical analyses
15 glow stick products were purchased in physical shops in August 2012 and in online stores from October-December 2012 and subsequently they were analysed. It was assessed that all purchased glow stick products can be used for gimmicks and gags and that they can appeal to children as toys. Prior to chemical analyses, the glow sticks were snapped and the liquid was analysed for selected solvents and oxidizing agents.

Investigations of the purchased glow sticks demonstrated that the liquid volume varied a lot; from less than 100 µl in the smallest glow sticks to app. 90 ml in the largest glow sticks.

Chemical analyses of the liquid in the 15 glow stick products revealed a content of butyl benzoate, 1,2,3-propantriol diacetate, dibutyl phthalate, dimethyl phthalate, tributyl acetyl citrate, tributyl citrate and triethyl citrate. The hydrogen peroxide concentration was between 0.4 and 2.4% in the investigated glow sticks.

Analyses of glow sticks show that 69 – 99% of the contents were composed of the solvents that were analysed for. Added to that comes the analysis for oxidizing agents (hydrogen peroxide) which resulted in the analysis in total accounting for minimum 70% of the chemical substances in glow sticks and in most cases more than 99% of the content. The final per cent consisted of the dye (app. 0.1%), one or several phenyl oxalate esters, e.g. CPPO (1-13.5%) and other chemical substances (<10%), e.g. solvents based on the content description acquired during the survey. Phenyl oxalate ester forms part of the chemical reaction that results in the dye becoming fluorescent.

In connection with six of the glow sticks, the survey did not disclose information about their contents. In seven out of nine cases, where information was available, the information from the survey did not correspond with the solvents identified in the screening analyses.

During the survey, information was collected about expected contents in nine of the 15 analysed products. When comparing the information with the results of the chemical analyses, the information is only roughly correct for two of the glow stick products. In the other glow stick products, considerable amounts were identified of a substance that had not been informed.

The contents were stated on the packaging of one of the glow stick products and they had been confirmed during the chemical analyses. The stated contents did not correspond with the information collected during the survey.

Assessment of results and health hazardous effects
In one of the products, dibutyl phthalate was found in considerable amounts. That substance must not be used in toys or gimmick and gag articles as according to classification it may damage fertility or the unborn child. The risk arises after repeated or longer exposure. Therefore, glow sticks are not believed to constitute an isolated risk but they contribute to the total exposure.

According to the order on prohibition of phthalates in toys and articles for younger children[1], dibutyl phthalate has been forbidden in products for children of up to 3 years of age since 2009 (limit value 0.05%). That means that the use of dibutyl phthalate in glow sticks, considered to be toys, is a violation of the law.

[1] https://www.retsinformation.dk/Forms/R0710.aspx?id=126137

Two of the most ordinary solvents found in glow sticks (dimethyl phthalate and butyl benzoate) can when swallowed or when they come into contact with the eyes cause a stinging sensation or discomfort. That is consistent with the descriptions of the symptoms after human exposure to liquid from glow stick products.

An official classification of dimethyl phthalate and butyl benzoate has not been carried out and therefore the classification has to be carried out by the manufacturer/supplier as a so-called self-classification.

Classifications from different suppliers can vary as they might have used different data or have interpreted the data differently. In ECHA's database of reported classifications, dimethyl phthalate is most frequently self-classified as ”not dangerous” and butyl benzoate is most frequently self-classified as ”dangerous” according to the CLP Regulation of the EU.

In the safety data sheets of the glow stick products, dimethyl phthalate and butyl benzoate are designated ”not dangerous” and none of the glow stick products are classified as ”dangerous”.

Hydrogen peroxide was not demonstrated in concentrations that involved the classification and labelling of the product. Butyl benzoate can have a skin irritating effect and could be the reason for the reported cases of irritated skin.

If dimethyl phthalate and butyl benzoate were not used in glow sticks, the acute effects observed after contact with the content would most likely be reduced significantly.

The analysed products demonstrated a substantial content of triethyl citrate, tributyl citrate, tributyl acetyl citrate and 1,2,3-propantriol diacetate in several of the products. The substances are not classified and do not constitute any known health risks.

Konklusion og sammenfatning

Knæklys - også kaldet glow sticks - er engangslys, som består af et plastrør eller anden beholder indeholdende to kemiske væsker, der danner en fluorescerende farve, når væskerne blandes.

I nærværende projekt undersøges knæklys som appellerer til børn, enten fordi de kan benyttes som legetøj, som spøg-og-skæmt-artikel eller som dekoration/smykke.

Lovgivning
Knæklys er omfattet af den europæiske kemikalielovgivning REACH. Produktgruppen knæklys betragtes under REACH som en kombination af en artikel og en "kemisk blanding i en beholder". Hvis produktet sælges til private forbrugere, må det ikke indeholde CMR-stoffer (kræftfremkaldende, mutagene eller reproduktionstoksiske stoffer) i koncentrationer, der medfører, at produktet som helhed skal klassificeres som enten kræftfremkaldende, mutagent eller reproduktionstoksisk. Hvis produktet anvendes til udsmykning, spøg og skæmt o.l., må produktet ikke indeholde flydende farlige stoffer eller blandinger i koncentrationer, der medfører, at produktet som helhed skal klassificeres som farligt.

Kemiske blandinger er omfattet af reglerne for klassificering, mærkning og emballering af farlige stoffer og blandinger (CLP-forordningen). Materialer, der indeholder stofblandinger med koncentrationer, som vurderes farlige for sundhed eller miljø, skal klassificeres og mærkes i henhold til forordningen.

Ifølge Legetøjsbekendtgørelsen må legetøj til børn op til tre år ikke indeholde farlige stoffer eller præparater, der kan skade sundheden for de børn, der bruger det. Der gælder særlige regler for visse ftalater i legetøj.

Vurdering af eksponering
Den hyppigste eksponering vurderes at være hudkontakt, indtagelse eller stænk i øjnene. Eksponeringen forventes kun at ske en eller få gange i et livsforløb.

Der findes ingen statistikker vedrørende eksponering for knæklys eller behandling efter uheld med knæklys fra Danmark, men Giftlinjen på Bispebjerg Hospital oplyser, at der modtages ca. 25 henvendelser om året vedrørende knæklys, ofte unge mennesker, som bider hul på dem. Der ses meget sjældent skader, men af og til lidt svien i mund og svælg. Astma-Allergi Danmark og Informationscenter for Miljø & Sundhed oplyser, at de ikke har registreret henvendelser vedrørende knæklys.

Resultater af kortlægningen
Kortlægningen omfatter alene knæklysprodukter, der markedsføres i Danmark, eller som forhandles på danske/dansksprogede internetsider med fokus på produkter, som er tiltænkt børn, eller som appellerer til børn, og derfor kan være både legetøj og spøg og skæmt artikler. Børn er defineret som børn under 14 år. Kortlægningen er gennemført i perioden juni-august 2012.

Ved besøg i en række detailhandelsbutikker og internetbutikker blev knæklys registreret i en del forskellige farver, hvoraf de mest udbredte er blå, rød, gul, grøn, pink og orange. Knæklys findes primært i butikkernes varesortiment som sæsonvare, fx i forbindelse med halloween og nytår. Der er primært tale om knæklysstave eller -pinde, hvor der medfølger samlemuffer til konstruktion af armbånd og halskæder. Knæklys findes også som en del af større samlesæt, hvor man ved hjælp af pinde, medfølgende samlemuffer og andre dele selv fremstiller fx "øreringe", "briller" og "kasketter".

Henvendelser til producenter/importører/forhandlere viste, at der er tale om et begrænset antal producenter af knæklys, og det er da også i stort omfang de samme produkter, man kan købe fx i internetbutikker. Der blev modtaget tilbagemeldinger med oplysninger om indholdsstoffer fra seks forskellige producenter.

Resultater af kemiske analyser
Der blev indkøbt og analyseret 15 knæklysprodukter i fysiske butikker i august 2012 og i netbutikker i oktober- december 2012. Det vurderes, at alle de indkøbte knæklysprodukter kan anvendes til spøg og skæmt, og at de kan appellere til børn som legetøj. Forud for analyserne blev knæklysene knækket, og væsken blev analyseret for udvalgte opløsningsmidler og oxiderende stoffer.

Undersøgelser af de købte knæklys viste, at væskevolumen var meget forskellig; fra under 100 µl i de mindste knæklys til ca. 90 ml i de største knæklys.

Der blev ved kemisk analyse af væsken i de 15 knæklysprodukter påvist indhold af butylbenzoat, 1,2,3-propantrioldiacetat, dibutylftalat, dimethylftalat, tributylacetylcitrat, tributylcitrat og triethylcitrat. Indholdet af hydrogenperoxid var mellem 0,4 og 2,4 % i de undersøgte knæklys.

Analyse af knæklys viser, at 69 – 99 % af indholdet udgøres af de opløsningsmidler, der er blevet analyseret for. Hertil kommer analysen for oxiderende stoffer (hydrogenperoxid), som resulterer i, at der samlet redegøres for minimum 70 % af de kemiske stoffer i knæklysene og i de fleste tilfælde mere end 99 % af indholdet. De sidste procent udgøres af farvestoffet (ca. 0,1 %), en eller flere phenyloxalatestre, fx CPPO (1-13,5 %) og andre kemiske stoffer (<10%) f.eks. opløsningsmidler vurderet ud fra oplysninger fremkommet ved kortlægningen. Phenyloxalatestre indgår i den kemiske reaktion, som medfører at farvestoffet kan fluorescere.

Under kortlægningen blev der indhentet informationer om forventede indholdsstoffer for ni af de 15 analyserede produkter. Ved sammenligning af disse oplysninger med resultaterne af de kemiske analyser er oplysningerne kun tilnærmelsesvis rigtige for to af knæklysprodukterne. I de øvrige knæklysprodukter blev der fundet betydelige mængder af et stof, som ikke var oplyst.

På emballagen til et af knæklysprodukterne var angivet indholdsstoffer, som senere blev påvist ved de kemiske analyser. De angivne indholdsstoffer svarede ikke overens med oplysningerne indhentet fra producenterne.

Vurdering af resultater og sundhedsskadelige effekter
I et af produkterne blev der fundet dibutylftalat i betydelige mængder. Dette stof må ikke anvendes i legetøj og spøg og skæmt-artikler, da det ifølge klassificeringen kan være skadelig for reproduktionen og kan have effekt på det ufødte barn. Risikoen opstår ved gentagen eller længerevarende eksponering. Knæklys vurderes således ikke at udgøre en isoleret risiko, men bidrager til den samlede eksponering.

I henhold til bekendtgørelse om forbud mod ftalater i legetøj og småbørnsartikler[2] er dibutylftalat siden 2009 forbudt i produkter til børn op til 3 år (grænseværdi 0,05 %). Anvendelsen af dibutylftalat i knæklys, der betragtes som legetøj, er således en overtrædelse af lovgivningen.

To af de mest almindelige opløsningsmidler, der er fundet i knæklys, dimethylftalat og butylbenzoat, kan ved indtagelse eller kontakt med øjnene, give anledning til svien og ubehag. Det passer med de beskrivelser, man kan finde, af symptomer ved eksponering af mennesker med væske fra knæklysprodukter.

Der er ikke foretaget en officiel klassificering af dimethylftalat og butylbenzoat, og klassificeringen skal derfor udføres af producenten/leverandøren i form af en såkaldt selvklassificering.

[2] https://www.retsinformation.dk/Forms/R0710.aspx?id=126137

Klassificeringer fra forskellige leverandører kan variere, da de kan have anvendt forskelligt datagrundlag eller fortolket data forskelligt. I ECHA's database over indrapporterede klassificeringer, er dimethylftalat hyppigst selvklassificeret som "ikke farlig" og butylbenzoat er hyppigst selvklassificeret som "farlig" i henhold til EU's CLP-forordning.

I sikkerhedsdatabladene for knæklysprodukterne er dimethylftalat og butylbenzoat betegnet "ikke farlige", og ingen af knæklysprodukterne er klassificeret som "farlige".

Hydrogenperoxid blev ikke påvist i koncentrationer, som bevirker, at produkterne skal klassificeres og mærkes.

Butylbenzoat kan have en hudirriterende effekt og kunne være årsag til de tilfælde af irriteret hud, der er rapporteret.

Hvis der ikke blev benyttet dimethylftalat og butylbenzoat i knæklys, ville de akutte effekter ved kontakt med indholdet formentlig kunne reduceres betragteligt.

I de analyserede produkter er der fundet triethylcitrat, tributylcitrat, tributylacetylcitrat og 1,2,3-propantriol-diacetate som en væsentlig bestanddel i flere af produkterne. Disse stoffer er ikke klassificeret og udgør ingen kendte sundhedsfarer.

1. Background

1.1 What glow sticks are used for

Glow sticks are disposable and consist of a plastic tube or other casing with another plastic tube or glass vial inside of it. The inner and outer tubes contain two chemical solutions that create a fluorescent light when they are combined by bending the plastic tube which makes the inner plastic tube or glass vial break. Glow sticks work by releasing chemical energy, not heat or gases, and therefore they can be used under pressure and batteries are not needed. Most often a glow stick lasts from 6 to 15 hours.

At the end of the 1960s, the chemical process on which the chemical reaction is based and which still is used in glow sticks was described for the first time by the chemist Edwin Chandross of Bell Labs. Several researchers continued Chandross´ work and few years later the first patents were issued on the content in glow sticks. One of the first patents on glow sticks was taken out by the US Navy in 1973[3].

Glow sticks were quickly introduced to the commercial market especially within recreation and they were later marketed for entertainment and as toys for children. As glow sticks do not release heat and at the same time are inexpensive their use has become widespread not least among children and young people.

Glow sticks are still used for business purposes, e.g. within the shipping trade and military forces and the police use glow sticks in connection with various operations. They e.g. use infrared glow sticks that require special equipment (e.g. night glass) to be seen.

Glow sticks are often used in connection with diving, fishing, orienteering and other recreation pastimes. Conventional glow sticks are especially used for special tasks such as light markers, light sources or as part of a safety procedure.

FIGURE 1.1 GLOW STICKS FOR SALE FOR DKK 5 AT A SCOUT CAMP IN THE DANISH TOWN CALLED HOLSTEBRO IN 2012 WHERE MORE THAN 35,000 CHILDREN FROM 6 YEARS OF AGE PARTICIPATED.

Concurrently with the spreading of glow sticks for entertainment and play, the use of glow sticks has changed. Fluorescent swords and luminous bracelets have become popular among children while luminous glasses, straws, glasses and hats have become part of the popular culture among young people. The last-mentioned products are also frequently used at children's birthday parties. The wrong use of glow sticks, e.g. storage in a freezer (in the wrong assumption that they will be reactivated), placing them in drinks or trying

[3] http://scholar.lib.vt.edu/theses/available/etd-5298-191116/unrestricted/cases2.pdf

to snap them again, increases the risk of puncturing the surrounding containers and with that increases the risk of contact with the chemicals in the tubes. Glow sticks for tongue piercings belong to the more exotic type of applications.

In connection with parties, an erroneous use of glow sticks has often been observed. Deliberately puncturing the glow stick and swallowing the contents are examples of what took place at the Roskilde Festival in 2009 where several people had to be admitted to hospital after swallowing the liquid from glow sticks and applying it to the skin.[4, 5, 6]

1.2 Composition and effect

The two substances in glow sticks contain several different chemical substances with different functions. The one substance is usually contained in a glass vial and it is surrounded by the other substance. The two substances are surrounded by a flexible material, typically a plastic tube. The vial is shattered by snapping the glow stick and then the two substances become mixed. As soon as the glow stick is activated by bending (”snapped” in this project) a chemical reaction takes place between some of the chemical substances in the glow stick which generates the desired fluorescent effect.

The two chemical substances that initiate the process by a chemical reaction are most frequently a diphenyl oxalate ester and peroxide (activator), typically hydrogen peroxide. The two chemical substances are physically separated until the glow stick is snapped. When the two chemical substances are mixed a chemical reaction takes place, releasing energy. The released energy is absorbed by a fluorescent dye and light is released. In addition to the reactive substances other chemical substances are presented as facilitators, including solvents.

An information retrieval identified 18 known diphenyl oxalate esters that are used for chemical luminescence either as pure substances or as mixtures of the various types.[7] The colour emitted from the glow stick is determined by which fluorescent dye has been used. An information retrieval localized many different fluorescent dyes used in chemiluminescent products.[3]

In addition, glow sticks contain solvents, e.g. phthalates, to dissolve the reactive chemical substances, to ensure solubility of the other chemical substances (e.g. dyes) and to distribute the solution in the glow stick. Previously, dibutyl phthalate (DBP) or similar phthalates were used as solvent in glow sticks. A leading manufacturer of glow sticks explains that their products now are phthalate-free.[8]

To make a glow stick work, the inner vial (most often of glass) has to be shattered and therefore the outer material is a very flexible plastic container. Softening agents might be added to the plastic material e.g. in the form of phthalates. Assessment and investigation of the outer material does not form part of this project.

[4] Hoffman, R. J., et al. 2002. Pediatric and Young Adult Exposure to Chemiluminescence Glow Sticks. Arch Ped. & Adolesc. Med. 1, 9, 2002.

[5] Garnier, R. et al. 2011. Expositions à des dispositifs luminescents: cas enregistrés par les centres antipoison et de toxicovigilance français. Rapport fait en réponse à la saisine de la Direction générale de la Santé. 2011

[6] http://go.tv2.dk/articlefornoejelse/id-23468465:festivalg%C3%A6ster-drikker-kn%C3%A6klys.html

[7] Patent application number: 20080308776; Chemiluminescent compositions and methods of making and using thereof, Bindra et al. 2008

[8] http://www.cyalume.eu/faq.html

1.3 Description of the chemical reaction

The chemical reaction in a glow stick takes place as hydrogen peroxide oxidizes a phenyl oxalate ester, yielding partly phenol and partly an unstable by-product called peroxy acid ester (a cyclic dimer of carbon dioxide). The unstable cyclic compound decomposes to carbon dioxide, releasing energy that excites the dye. The excited electrons in the fluorescent dye jump to a higher energy level and then fall back and release light. The process was patented in 1973 [9] and is called cyalume, see Figure 1.2.

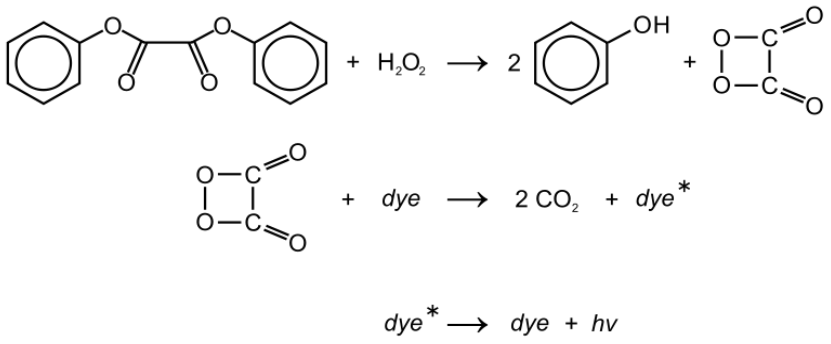

FIGURE 1.2 SCHEMATIC DIAGRAM OF THE CHEMICAL PROCESS IN A GLOW STICK[10]

Different types of ester are used as initial substance e.g. substituted with methyl groups making it possible to create different phenols.

An information retrieval identified a number of different fluorescent dyes that can appear in glow sticks, see examples in Table 1.1 example of fluorescent dyes that can appear in glow sticks[11, 12].

No.	Name	CAS no.	Colour at emission
1	9,10-diphenylanthracene (DPA)	1499-10-1	Blue
2	1-chlor-9,10-diphenylanthracene	43217-27-2	Yellow-green
3	2-chlor-9,10-diphenylanthracene	43217-28-3	Blue-green
4	9,10-bis(phenylethynyl)anthracene	10075-85-1	Yellow-green
5	1-chlor-9,10-bis(phenylethynyl)anthracene	41105-35-5	Yellow-green
6	2-chlor-9,10-bis(phenylethynyl)anthracene	41105-36-6	Green
7	1,8-dichloro-9,10-bis(phenylethynyl)anthracene	51749-83-8	Yellow
8	Rubrene	517-51-1	Orange-yellow
9	2,4-di-tert-butylphenyl 1,4,5,8-tetracarboxynaphthalene diamide	30431-54-0	Red
10	Rhodamine B	81-88-9	Red
11	5,12-bis(phenylethynyl)naphthacene	18826-29-4	Orange

[9] http://scholar.lib.vt.edu/theses/available/etd-5298-191116/unrestricted/cases2.pdf
[10] http://www.nationmaster.com/encyclopedia/Lightstick
[11] Patent application number: 20080308776; Chemiluminescent compositions and methods of making and using thereof, Bindra et al. 2008
[12] Patent application number20110017091; Combined thermal and Chemiluminescent reaction system; Cranor et al. 2011

No.	Name	CAS no.	Colour at emission
12	Violanthrone-79	85652-50-2	Orange
13	16,17-(1,2-ethylenedioxy)violanthrone	-	Red
14	16,17-dihexyloxyviolanthrone	25637-03-0	Infrared
15	16,17-butyloxyviolanthrone	85652-51-3	Infrared
16	N,N'-bis(2,5,-di-tert-butylphenyl)-3,4,9,10-perylendicarboximide	83054-80-2	Infrared
17	1-N,N-dibutylaminoanthracene		Infrared
18	6-methylacridinium iodide	948-43-6	Infrared

TABLE 1.1 EXAMPLE OF FLUORESCENT DYES THAT CAN APPEAR IN GLOW STICKS

1.4 Legislation

Different rules apply depending on the marketing, appearance and application of the product. General rules apply to articles and chemical products and special rules apply to products that are used for gimmicks and gags and as toys.

In this project, glow sticks intended for children or glow sticks that appeal to children were investigated. The glow sticks can be regarded as gimmick and gag articles and/or toys.

1.4.1 REACH

Glow sticks fall within the European Community Regulation on chemicals called REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances). According to REACH, glow sticks belong to the product group that is a combination of an article and ”a chemical mixture in a container”.

If the product is sold to private consumers it must not contain CMR substances (carcinogenic, mutagenic or toxic for reproduction) in concentrations that require classification of the product as carcinogenic, mutagenic or toxic for reproduction (cf. REACH, enclosure XVII, no. 28-30). If the product is used for personal ornamentation, gimmicks and gags or the like, then the product must not contain fluid dangerous substances or mixtures in concentrations that require classification of the product as dangerous (cf. REACH enclosure XVII, no. 3)[13].

According to REACH, diethylhexyl phthalate, dibutyl phthalate and benzyl butyl phthalate have since 16 January 2007 been forbidden in the EU in toys and articles for children of up to the age of 14 with a limit of 0.1%, while diisononyl phthalate, di-n-octyl phthalate and diisodecyl phthalate have been forbidden in the EU in all toys and articles for children that can be put in the mouth with a limit of 0.1% since 16 January 2007.

1.4.2 CLP

Chemical mixtures are comprised by the regulations on classification, labelling and packaging of dangerous substances and mixtures (CLP Regulation). The classification assesses the properties of a substance in relation to environmental, human health and physical dangers. Hazardous substances or mixtures in concentrations that are assessed to be dangerous must be labelled with a danger pictogram as well as hazard and safety sentences according to the labelling rules of the regulation.

[13] Questions and answers to ECHA help desk (HELPEX ID 11801)

The CLP Regulation is being phased in, and therefore transitional rules apply for mixtures until June 2015. During the transitional period, a mixture can be either classified & labelled according to the Executive Order on Classification[14] or according to the CLP Regulation. In connection with mixtures, classification of the individual substances must be stated according to both protocols on the data safety sheet up to June 2015. However, on the label, the mixture (the product) only has to be marked according to one protocol.

1.4.3 Toys

According to the Executive Order on Toys[15], there must be no risk of harmful effects to human health after exposure to the chemical substances and mixtures in the toy. In Denmark, special rules apply to certain phthalates in toys and articles for children (Executive Order 855 of 05/09/2009). Phthalates are forbidden in toys and articles for children less than three years of age with a limit of 0.05%.

After 1 December 2013, dibutyl phthalate, diethylhexyl phthalate, diisobutyl phthalate and benzyl butyl phthalate will be forbidden in consumer products that are stored indoors or that can come into touch with the skin and mucous membranes with a limit value of 0.1%[16].

[14] Executive Order No. 1075 of 24/11/2011
[15] Executive Order No. 13 of 10/01/2011
[16] Executive Order No. 1113 of 26/11/2012

2. Survey

2.1 Objective of the survey

The objective of the survey was to identify consumer products on the Danish market within the product group called glow sticks that are aimed at children or that appeal to children and that would be regarded as toys and/or gimmick and gag articles.

2.2 Delimitation

The survey only comprised glow stick products that are marketed in Denmark or that are sold on Danish/ Danish-language internet pages.

In addition, the survey is limited to products where two liquids are mixed so a fluorescent liquid is created with an effect that lasts between six and 15 hours.

Focus has solely been on products where children are expected to be the target group. That means products that are intended for children or that appeal to children. Children are defined as children less than 14 years of age in accordance with the Executive Order on safety requirements to toy products[17].

2.3 Procedure

The survey was carried out in the period from June-August 2012.

Visits were paid to a number of retail shops as well as to a number of online stores dealing with glow sticks. In addition, one festival, a scout camp and an amusement park were visited.
A written inquiry was sent to a number of Danish chain shops concerning glow stick products for children.

The Poison Control Hotline at Bispebjerg Hospital, Asthma-Allergy in Denmark, the Information Centre on Environment and Health and the Danish Consumer Council were contacted in order to obtain information about whether the organisations have registered inquiries concerning the use of glow sticks or not.

2.3.1 Shop visits

A total of 28 shops were visited, including:

- Toy shops
- Bookshops
- Discount shops
- Supermarkets
- Department stores
- DIY centres
- Sports shops
- Joke shops
- Souvenir shops
- Hardware shops.

Visits were also paid to one festival, a scout camp and an amusement park and advertisements etc. were studied to find shops that sell glow sticks.

[17] Executive Order on safety requirements to toy products No. 13 of 10 January 2011

2.3.2 Internet visits

Searching took place on Google with different search words such as e.g. ”Glowsticks”, ”Glow sticks”, ”Glow lights”, ”Halloween”, ”toys”, ”children” and combinations thereof.

2.3.3 Inquiries to manufacturers/importers/distributors

The manufacturers/importers/distributors of the glow stick products that were registered during shop visits and via internet pages were contacted. Contact consisted of an informative letter and a questionnaire that were prepared in Danish. In two cases, the material was prepared in English so it could be sent to foreign manufacturers.

Four types of inquiries were in question:

- General inquiries to companies that were regarded as possible distributors of glow stick products (see Appendix 1).
- Inquiries to companies whose products were registered in retail shops (see Appendix 2). Material was prepared in Danish and English.
- Inquiries to online stores where the survey demonstrated sale of products aimed at children or that could appeal to children (see Appendix 3).
- Inquiries to manufacturers and importers (see Appendix 4). Material was prepared in Danish and English.

General contact was taken to a number of Danish chain shops.

2.4 Result of the survey

2.4.1 Result of general inquiries

The general inquiry to a number of national chain shops consisted of an informative letter and a questionnaire. The questionnaire contained questions about whether or not the company sells glow stick products to children. If so, they were asked if seasonal goods are in question, or if the product range is available all year round. In addition, the companies were asked to give information about the manufacturer/importer and if they had specific information about the content of the products, if possible in the form of safety data sheets.

New contact was taken to the companies that did not respond to the first inquiry.

In total, 26 replies to 27 inquiries were received. See Appendix 6 for an outline of the Danish chain shops that were contacted.

27% of the contacted chain shops informed that they sell glow stick products to children, while 73% informed that they do not.

Out of the seven companies that informed that they sell glow stick products to children, two companies (corresponding to 29%) informed that glow stick products are a fixed part of their product range. The other five companies (corresponding to 71%) informed that glow stick products only periodically form part of their product range – for instance in connection with Halloween and New Year’s Eve.

2.4.2 Result of retail shop visits

Only a few of the retail shops that were visited, sold glow stick products during the survey period (June-August).

A total of 28 retail shops, booths at a festival, a scout camp and a shop in an amusement park were visited and glow stick products were only registered at nine places.

Glow stick products were registered the following places:

- Bookshop
- Souvenir shop
- Supermarket
- Discount shops
- DIY centre
- Joke shops
- Scout camp
- Amusement park.

In several of the shops that were visited, the staff said that they currently did not sell glow stick products and that glow stick products typically form part of the product range during Halloween and New Year's Eve.

Some of the visited retail shops formed part of a chain. Although several shops within a specific chain were visited, they are only registered as one shop in the specification.

The glow stick products that were registered when visiting the retail shops were mainly rods or sticks with connectors for making bracelets or necklaces and larger assembly kits with which you make your own e.g. ”earrings”, ”glasses” and ”caps” with the enclosed sticks, connectors and other parts.

As part of the survey, selected shops, where glow sticks were registered, were subsequently contacted in writing. The shops received an informative letter and a questionnaire. A new inquiry was sent to the companies that did not respond to the first inquiry.

Contact was taken to a total of four shops and two shops replied.

One shop said that glow sticks for children form part of the fixed product range whereas the other said the products only periodically form part of the product range.

Glow stick products were not registered at the festival that was visited, but one product was registered at the scout camp and the amusement park, respectively.

2.4.3 Result of survey via internet pages

During the survey via internet pages, a number of websites offering glow stick products were registered. However, mainly the same type of products were in question, e.g. bracelets, glasses, straws etc.

The registered online stores were contacted with a questionnaire. Also in these cases, contact was once again taken to the shops that did not respond to the first inquiry.

Contact was taken to 28 online stores and nine shops replied. Among them, 33% said that glow stick products for children do form part of the fixed product range, while 67% said that they do not form part of the fixed product range.

2.4.4 Result of inquiries to manufacturers/importers

The manufacturers/importers, which partly appeared through general inquiries, inquiries to retail shops and online stores and partly appeared from the information on the product itself, were contacted.

The informative letter and questionnaire were sent to 10 manufacturers/importers and five of them answered the inquiry. 80% said that glow sticks for children form part of their fixed product range, while 20% said the products only periodically form part of the product range.

2.4.5 Result of inquiry about composition and content

Inquiries to manufacturers/importers/distributors resulted in responses with information about contents from six different manufacturers.

The responses confirm that glow sticks consist of two liquids that are separated until the product is snapped. Some manufacturers call the two liquids for activator and colour solution, respectively, and the activator contains hydrogen peroxide. According to information about the content in glow sticks that appeared during the survey, there are in addition to variation in dyes also differences in the solvent composition in the liquid in the glass vial and the liquid surrounding the vial, respectively.

7 different glow stick manufacturers were identified, but glow sticks were also found where information about the manufacturer could not be obtained.

2.4.6 Result of inquiries to organisations

In order to find out if the organisations have registered inquiries regarding the use of glow sticks, the Poison Control Hotline, Asthma-Allergy Denmark, the Information Centre on Environment and Health and the Danish Consumer Council were contacted.

Three of the four organisations responded to the inquiry.

The Poison Control Hotline states that they annually receive app. 25 inquiries that concern glow sticks. Usually, young people who bite a hole in the product are in question. Injuries arising in that connection are rarely reported; however, sometimes a stinging sensation has been reported in mouth and throat.

On the website of the Poison Control Hotline – end of August – glow sticks were mentioned on the list of most read pages. On the website of the Poison Control Hotline, the following text about glow sticks appears: ”Risk: Plastic tubes that become luminescent when the tube is snapped. Originally fishing equipment but has been used as glow sticks at discos. The content is i.a. a small amount of fluorescent liquid and hydrogen peroxide. Can give stomach/bowel irritation after swallowing. Precautions: After swallowing: Drink some kind of fluid.”[18]

Asthma-Allergy Denmark informs that they have not registered inquiries concerning glow sticks. The same goes for the Information Centre on Environment and Health.

[18] http://www.bispebjerghospital.dk/cgi-bin/MsmGo.exe?grab_id=0&page_id=916&query=kn%C3%A6klys&hiword=KN%C3%A6KLYDE%20kn%C3%A6klys%20

2.5 Total result of the survey

Glow sticks were registered in a number of different colours. The most common are blue, red, yellow, green, pink and orange.

Inquiries to retail shops showed that glow sticks mainly are available in the product range of the shops as seasonal goods, e.g. in connection with Halloween and New Year's Eve.

The survey demonstrated that glow sticks for children or glow sticks that appeal to children to a great extent are the same product. There is mainly talk of sticks or rods where connectors are included so bracelets and necklaces can be made. Glow sticks also exist as part of larger assembly kits with which it is possible to make your own "earrings", "glasses" or "caps" by using the enclosed sticks, connectors and other parts.

Inquiries to manufacturers/importers/distributors showed that there is talk of a limited number of manufacturers of glow sticks and to a great extent the same products can e.g. be purchased in online stores.

Inquiries to manufacturers/importers/distributors resulted in responses with information about contents from six different manufacturers.

The Poison Control Hotline informed that they receive app. 25 inquiries a year concerning glow sticks. Asthma-Allergy Denmark and the Information Centre on Environment and Health stated that they have not registered inquiries regarding glow sticks.

3. Exposure

3.1 Citizen inquiries regarding glow sticks

An assessment of realistic worst case exposure scenarios for children's use of glow sticks was carried out. The assessment comprises descriptions of reported cases of exposure.

No Danish statistics exist regarding exposure to glow sticks or treatment after accidents with glow sticks, but the Poison Control Hotline at Bispebjerg Hospital has informed that app. 25 inquiries are received annually concerning glow sticks; often from young people who have bitten a hole in them. Injuries are seldom, but now and then stinging sensations in mouth and throat are seen. In that connection, the internal guidelines of the Poison Control Hotline refer "toxicological" to hydrogen peroxide.[19]

Asthma-Allergy Denmark and the Information Centre on Environment and Health state that they have not registered inquiries regarding glow sticks.

A French report estimated the number of reported contacts with luminescent products over a 12-year period from 1999 – 2010[20]. In total, 2.029.714 exposed persons in France were registered. The number of registrations per year increased exponentially during that period. There is an obvious hyper-frequency in connection with summer, Christmas and weekends. Children from 1-4 years and 5-9 years constitute app. 50% and 37%, respectively, of all cases. In 2.979 of the cases (app. 1.5‰), symptoms were registered. 85% were categorised as oral exposure, 13% as eye exposure and 5% as skin exposure.

In an American report on exposure to glow sticks[21] (registered at a poison centre in the US), oral intake amounted to 91.5% of the cases, eye exposure to 7.6% and skin contact to 0.9%. 96 out of 118 cases were children from 0 – 12 years. The patients only developed symptoms if they had been exposed to the liquid in glow sticks.

The inferior number of cases with registered symptoms indicates that people seek help when they suspect that the liquid might be hazardous to health, more often than because they have experienced certain symptoms. It is easy to imagine that especially parents to younger children become worried. That probably partly explains the high frequency of children in the statistics of inquiries to poison centres/casualty wards. Children probably frequently appear in the statistics as glow sticks appeal to children and there is a great risk that they might use glow sticks incorrectly.

[19] http://www.bispebjerghospital.dk/giftlinjen/forside/

[20] Garnier, R. et al. 2011. Expositions à des dispositifs luminescents: cas enregistrés par les centres antipoison et de toxicovigilance français. Rapport fait en réponse à la saisine de la Direction générale de la Santé. 2011

[21] Hoffman, R. J., et al. 2002. Pediatric and Young Adult Exposure to Chemiluminescence Glow Sticks. Arch Ped. & Adolesc. Med. 1, 9, 2002.

3.2 Ways of exposure when using glow sticks

On the basis of the above registered citizen inquiries and a general reflection on how glow sticks can be expected to be used by children, the following are examples of situations where there is risk of exposure to the contents:

1. During snapping when the outer material breaks and the liquid splashes onto the skin and in the eyes. It is assumed that only a small part of the liquid comes into contact with the skin or eyes.
2. After snapping 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 assumed that the worst case scenario would be the risk of swallowing the entire content or getting the entire content on the skin or possibly splashes in the eyes.
3. After snapping and while the product is luminous, when a hole intentionally is cut in the product in order to pour the contents onto the skin, clothes or something else. It is assumed that the worst case scenario would be that the entire content is swallowed or comes into contact with the skin.
4. When the product, after snapping and while it is luminous is put in the freezer (e.g. due to the incorrect impression that the reaction can be stopped) and then once again trying to snap it, risking damage to the outer material. The worst case scenario corresponds to item 3.

Assessment of exposure from the outer material and assessment of the risk of exposure to glass fragments from the glass vial do not form part of this project.

In the following, various types of exposure are studied.

3.2.1 Dermal exposure

When breaking the containers with the chemical, the liquid will often run out onto the skin and clothes.

In cases where exposure takes place due to accidents or unintentional use, the max. dose is assessed to correspond to the total volume of liquid in a glow stick. Repeated exposure within a shorter period of time is considered less likely.

3.2.2 Eye exposure

Eye exposure can arise due to splashes when breaking the container or if the glow stick is carried on the head or face (e.g. caps and glasses). In case of accidents or unintentional use, maximum exposure is assumed to constitute a sub-amount of the volume of the glow stick. Repeated exposure within a shorter period of time is considered to be less likely.

3.2.3 Oral exposure

Oral exposure arises due to intentional or unintentional ingestion of the liquid from a product that e.g. has been opened or cracked or in some other way leaks.

It is assumed that the worst case scenario in connection with unintentional ingestion is when the entire volume of liquid from a glow stick is swallowed. Repeated exposure during unintentional ingestion within a shorter period of time is considered to be less likely.

3.2.4 Inhalation

Exposure via inhalation is assumed to constitute an inferior risk due to the physical-chemical properties of the involved chemicals and due to the use of the products. No cases of exposure via inhalation have been described in literature.

4. Health assessment of contents

4.1 Classification procedure

The regulation called REACH[22] (Registration, Evaluation, Authorisation and Restriction of Chemical substances) and the regulation called CLP[23] (Classification, Labelling and Packaging) require that the chemical companies submit information on the substances they manufacture or import. That includes information on the hazard properties of the substances that constitute a risk to human health or the environment and on the possible (self)-classification of the substance according to the CLP Regulation.

As classification is based on toxicological investigations, uncertainty and judgement can be attached to the process due to different investigation results, different interpretations as well as different access to data. Several thousand companies, called notifiers, might have forwarded notifications. A number of substances have a harmonised classification that appears from enclosure VI of the CLP Regulation (List of Harmonized Classifications). Harmonised classification is obligatory at Community level and cannot be deviated from. Other substances are self-classified by the companies that market the substances. The companies must self-classify and report (notify) their self-classification to the European Chemicals Agency (ECHA)[24]. In connection with substances that solely are self-classified this report states the classification that most companies (notifiers) have informed.

It is necessary to note that the most frequent self-classification not necessarily is the most correct, but a more thorough investigation of all information on the health effects of the substances is not within the framework of this project. Information on the reported self-classifications and on substances with harmonised classification appears in the database *The Classification and Labelling Inventory* which is accessible on ECHA's website. [24]

In the CLP Regulation, the health effects are divided into danger classes and they have been assigned general concentration limits. Specific concentration limits might have been set for substances with harmonised classification and they have to be used instead of the generic concentration limits.[24] In connection with substances that do not appear in the ECHA database, safety data sheets were requested from larger chemical distributors and information was looked for on the Danish Environmental Protection Agency's guideline for self-classification of hazardous substances.

4.2 Classification of contents in glow sticks

Table 4.1 gives information about names and content concentrations in glow sticks. The information was received during the survey in connection with inquiries for composition and content. The shown classifications are stated in accordance with the CLP Regulation. The classification procedure with source reference is described in chapter 4.1.

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[22] REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

[23] REGULATION (EC) No 1272/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006

[24] http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory

Hydrogen peroxide has specific concentration limits for when the substance will generate classification of a mixture. The lower classification limit is when the mixture is 5 – 8%, which will result in classification and labelling for irritation of the eyes. In connection with the other contents, the general concentration limits apply.[24]

CAS no.	Substance	Concen-tration (%)	Source of classification[1)]	Danger class	H sentence[2)]
54-21-7	Sodium salicylate	0-0.005	Self-classified	Acute tox 4, eye irrit 2	H302, H319
75-65-0	2-Methyl-2-propanol (tert-butyl-alcohol)	0-2	Harmonised	Flam. liq. 2, eye irrit 2, acute tox 4, stot see 3	H225, H319, H332, H335
77-90-7	Tributyl acetyl citrate	0-40	Self-classified*	Not classified*	
77-93-0	Triethyl citrate	0-70	Self-classified	Not classified*	
128-37-0	2,6-di-terbutyl-p-cresol	0-0.015	Self-classified	Not classified* aquatic acute 1 aquatic chronic 1	H400 H410
131-11-3	Dimethyl phtha-late	0-99	Self-classified	Not classified*	
136-60-7	Butyl benzoate	0-45	Self-classified	Skin irrit 2 eye irrit 2	H315, H319
7722-84-1	Hydrogen - peroxide	0.05-1.2	Harmonised	Ox. liq. 1 eye irrit 2 (5-8%) skin corr. 1a, acute tox 4	H271, H302, H314, H332
30431-54-0	CPPO: Bis(3,4,6-trichlor-2-carbopentoxy-phenyl)oxalate	0-13.5	Self-classified	acute tox 4, acute tox 4, acute tox 4	H302, H312, H332
75203-51-9	CPPO: Bis(2,4,5-trichlor-6-carbopentoxyphe nyl)oxalate	1-13.5		*Substance does not appear in ECHS's database*	

TABLE 4.1 CLASSIFICATION OF CONTENTS AND SOURCES OF CLASSIFICATION

1. Source of classification:
   Self-classification: Most frequently applied self-classification according to ECHA's Classification and Labelling Inventory.
   * According to the ECHA database, most companies that have reported the substance have stated "not classified".

2. H sentence: H225 Highly flammable liquid and vapour; H271 May cause fire or explosion; strong oxidizer; H302 Dangerous to ingest; H312 Dangerous during skin contact; H314 Causes severe burns of skin and eye damages, H315 Causes skin irritation; H319 Causes serious eye irritation; H332 Dangerous to inhale; H335 Can cause irritation of the respiratory passages; H400 Very toxic to aquatic life; H410 Very toxic to aquatic life with long lasting effects.

According to the possible types of exposure described in paragraph 3.2, the realistic worst case scenario is that the contents are swallowed, poured onto the skin or splashed into the eyes. A realistic scenario would be exposure to glow stick liquid only once or a few times in a lifetime. Therefore, long-term exposure is not assessed. With a starting point in the worst case scenario, contents with high concentrations or with known acute toxicological effects were decided to be the focus of this survey.

On the basis of the above criteria, the following five substances were assessed to be the most interesting substances due to their expected concentrations in glow sticks or their toxicological profile (see Table 4.1 and Appendix 8):

- Butyl benzoate
- Dimethyl phthalate
- Hydrogen peroxide
- Tributyl acetyl citrate
- Triethyl citrate.

5. Choice of glow sticks for analyses

5.1 Criteria for purchase of products

In consultation with the Danish Environmental Protection Agency the following criteria were chosen for choice of glow sticks that were to be purchased and analysed (order of priority):

- Different manufacturers
- Glow sticks from physical shops as well as online stores
- Different designs that appeal to children
- Different sizes in order to estimate the volume of the liquid
- Larger products e.g. rods due to an expected high volume of chemicals constituting a high exposure risk.
- Different colours.

5.2 Outline of purchased glow sticks

Information on the purchased glow sticks appears from Table 5.1. Purchase of glow sticks mainly took place in physical shops in August 2012 and in online stores in October-December 2012.

Product no.	Product description	Type of shop	No. of glow sticks in package	Price	CE marked	Not recom-mended for age
1	Mask: Plastic mask and glow sticks	Discount shop	4	11.84 DKK	yes	0-3
2	Bracelet with plastic connectors	Bookshop	12	16.66 DKK	yes	0-3
3	Stick with string	DIY centre	1	9.95 DKK	no	Child's head with line through
4	Bracelet with plastic connectors	Joke shop	15	29.50 DKK	yes	0-3
5	Earrings: Plastic piece and glow sticks	Discount shop	20	30 DKK	yes	0-4
6	Sticks with string	DIY centre	1	9.95 DKK	yes	0-5
7	Sticks	Online store	4	54.95 DKK	yes	0-3
8	Mouth cover: Plastic piece and glow sticks	Online store	1	12.50 DKK	yes	0-5

Product no.	Product description	Type of shop	No. of glow sticks in package	Price	CE marked	Not recom-mended for age
9	Glasses: Plastic side bars and glow sticks	Online store	4	9.50 DKK	yes	0-3
10	Giant glow rod	Online store	1	25 DKK	no	0-5
11	Whistle: Plastic piece, glow sticks and string	Online store	1	5 DKK	yes	0-3
12	Straw: plastic pipe with glow sticks	Online store	6	6 DKK	yes	0-3
13	Clapping hands: glow sticks with plastic hand	Online store	12	10 DKK	yes	0-3
14	Sticks	Online store	10	70 DKK	yes	0-5
15	Bracelet with plastic connectors	Online store	50	79 DKK	no	Not declared

TABLE 5.1 OUTLINE OF PURCHASED GLOW STICKS

Some of the products had different colours in the same package.

5.3 Labelling of packaging

Appendix 9 states the registered text and labelling of packaging from the glow sticks. One product (no. 15) had no text on the packaging.

It is immediately assessed that all the purchased glow stick products can be used for gimmick and gag articles and that they can appeal to children as toys. However, the assessment of the Danish Safety Technology Authority determines if the glow sticks are toys. 13 of the products had a label stating that they are not recommended for children of a certain age (eight are advised against under 3 years, one is advised against under 4 years and four are advised against for children under 5 years of age). One product has a pictogram in the shape of a child's head with a line through.

On all 14 products with text on the packaging it was stated that contact should be avoided with eyes and skin and that contact can result in irritation. Furthermore, on 13 products it was written that the content must not be eaten or swallowed. On several of the products it was written that they must not be exposed to light or high temperatures.

On one product (no. 2) it was written which chemical substances the product contains. However, the information did not correspond with the information that appeared during the survey after communication with distributors and manufacturers.

6. Chemical analyses

6.1 Choice of chemical analyses

On the basis of information on expected contents in glow sticks and the classification of the substances (see Chapter 4 and Appendix 8) it was in consultation with the Danish Environmental Protection Agency decided to analyse glow sticks for the following four solvents that were expected to be present in high concentrations (see Appendix 7 and 8):

- Butyl benzoate
- Dimethyl phthalate
- Triethyl citrate
- Tributyl acetyl citrate.

A decision was made to start with a GC-MS screening analysis to investigate if other chemical substances were present in high concentrations that would be relevant to include in the subsequent quantitative analyses.

In addition, it was decided to carry out an analysis for hydrogen peroxide before the product is snapped, to investigate if the content corresponds with the information that appeared during the survey of an expected content from 0.05-1.2%. The applied analysis was not specific as it analyses for all oxidizing agents. However, as all the information received during the survey states that the glow sticks contain hydrogen peroxide it is assumed that the substance is the most applied oxidizing agent in glow sticks.

The GC-MS screening did not identify or quantify phenyl oxalate esters, e.g. CPPO. For that purpose HPLC has to be used and in consultation with the Danish Environmental Protection Agency it was decided that it should not form part of this project. Concentrations of phenyl oxalate esters were expected to be low (0-13.5% according to information from the survey, see Appendix 7), compared with the other solvents chosen for analysis, and phenyl oxalate esters will react with hydrogen peroxide when snapped and be converted to other chemical substances, see Figure 1.2.

6.2 Criteria for sampling sub-samples for analyses

Practical experience in the project demonstrated that the products glow quickly after snapping as the two substances are mixed and luminosity declines after some hours. A momentary reaction takes place and it reaches its maximum after a rather short time. Then the fluorescent reaction decreases until the glow stick cannot fluoresce several hours later.

During the quick initial reaction, there is a risk of contact with chemical substances from both liquids and with new chemical compounds that are produced through the chemical reaction after snapping. However, the reaction phase is estimated to constitute a small risk due to the short duration.

It is assessed that the solvents selected for analysis do not form part of the chemical reaction and they are only to a limited degree photochemically degradable and therefore the solvents are stable for more than 24 hours.

The glow sticks were snapped at least 24 hours before sub-samples were taken for analyses. That time span was chosen to ensure that all reactions in the glow sticks had ended.

As the chemical substances selected for analyses are solvents it was assumed that glow stick products in the same product package would contain the same solvents irrespective of colour.

In order to carry out the analysis for hydrogen peroxide, it was necessary to open the product without breaking the inner vial that starts the chemical reaction. Therefore, it was not possible to carry out the analysis on all products. Products with small dimensions could not be analysed.

6.3 Applied analysis methods

The following chapters describe the analysis methods that were used for analysing the content of glow sticks.

6.3.1 Method for determining content of oxidizing agents

Hydrogen peroxide was determined through a titration analysis. The applied analysis is not specific as it analyses for all oxidizing agents.

The applied method is the standard method ISO 6353/2-1983 (E) R 14 Hydrogen peroxide.

0.20 g liquid was weighed and mixed with 50 ml water and 20 ml sulphuric acid solution (16%). Titration took place with a 0.1 mol/l potassium permanganate solution till the colour turned pink.

The content of hydrogen peroxide was calculated on the basis of the applied amount of potassium permanganate solution as 1.00 ml of a 0.1 mol/l potassium permanganate solution corresponds to 1.7007 mg hydrogen peroxide.

6.3.2 GC-MS screening method

High concentrations of solvents in the purchased glow sticks were initially determined through a GC-MS screening and identification was carried out by comparing the mass spectrum with a NIST MS library. The applied screening method made it possible to identify volatile organic chemical substances that appeared in concentrations exceeding app. 5% as the samples were diluted before analysis.

The glow sticks were snapped and after at least 24 hours a sub-sample amount of the liquid was diluted with dichlormethane. Deuterium marked dimethyl phthalate was added as internal standard. Subsequently, a GC-MS screening was carried out.

The conditions of the GC-MS screening are stated in Table 6.1.

Equipment	Agilent GC (7890A) with MSD (5975C)
Column	Zebron ZB-5 MS 30 m x 0.25 mm x 0.25 µm
Injector	Split 25:1, 275 degrees
Oven settings	40-320 °C, 20 °C per min.
Mass spectrometer	Scan-mode, m/z 40-290

TABLE 6.1 GC-MS CONDITIONS

6.3.3 GC-MS quantitative method

After the glow stick content had been screened, a number of chemical substances were selected and the contents were quantified against external reference standards of the selected substances.

Two of each glow stick product was snapped (analysis in duplicate). 24 hours after the glow sticks had been snapped a sub-sample was taken of each glow stick and it was diluted with dichlormethane. Deuterium marked dimethyl phthalate was added as internal standard. Subsequently, a GC-MS screening was carried out. The conditions of the GC-MS quantification are stated in Table 6.2.

Equipment	Agilent GC (7890A) with MSD (5975C)
Column	Zebron ZB-5 MS 30 m x 0.25 mm x 0.25 µm
Injector	Splitless, 275 degrees
Oven program	40-320 °C, 20 °C per min.
Mass spectrometer	SIM-mode, m/z 40-290

TABLE 6.2 GC-MS CONDITIONS

6.3.4 Method validation of GC-MS quantitative method

A validation of the applied method for quantification was carried out.

In connection with the screening analyses as well as the quantitative analyses, a reference standard was included for all investigated chemical substances to carry out identification with retention time and mass spectra in addition to comparison of the mass spectrum with NIST MS library. The reference standards were prepared on the basis of chemicals purchased from Sigma-Aldrich.

Deuterium marked dimethyl phthalate was added as internal standard to compensate for possible variations in the GC-MS analysis.

Linearity of the measurement area was investigated by analysing the reference standard on two different days and at least at 5 different concentration levels.

Blank specimens were included in all analyses and no blank values were demonstrated for any of the analysed reference standards.

The detection limit was not investigated. That was irrelevant as all the investigated chemical substances exist in concentrations that by far exceed the detection limit of the equipment.

In connection with the quantitative analyses it was necessary to dilute between 2500-12500 times. Six sub-samples were taken of a glow stick where the necessary dilutions were carried out and subsequently analysed by GC-MS. With a starting point in the relative standard deviations, the repeatability of the method was calculated to 11%.

A recovery investigation was carried out by spiking six sub-samples of a glow stick with 1,2,3-propantriol diacetate, tributyl acetyl citrate and dimethyl phthalate. The recovery averages appear in Table 6.3. The results are within 100% ± 11%.

Name	Recovery (%)
1,2,3-propanetriol diacetate	109
Dimethyl phthalate	104
Tributyl acetyl citrate	98

TABLE 6.3 RESULTS OF RECOVERY, QUANTITATIVE GC-MS METHOD

6.4 Results of chemical analyses

In the following, the analysis results of the chosen glow sticks are described.

6.4.1 Visual observations of glow sticks

All of the glow sticks consisted of two tubes, where one tube was located inside the other tube. The inner tube contained a coloured liquid while the outer tube contained a clear liquid.

The length of the glow sticks was measured. The colour before snapping and the colour after snapping (time: 0-hours) and after app. 24 hours (time: 24-hours) was recorded. The results appear in Table 6.4. If the same colours were recorded at 0-hours and 24-hours, then that indicates that the colour remained unchanged after 24 hours.

When removing a sub-sample for analysis the total volume of the liquids in both tubes from the glow sticks was estimated. The total liquid volume in the glow sticks turned out to be very different; from less than 100 µl in the smallest glow stick to app. 90 ml in the largest glow stick. It was estimated that 5-10% of the liquid was left either on the inside of the outer material or on piece of broken glass which has not been included. The results appear in Table 6.4.

Product no.	Colour before snapping	Colour immediately after snapping (0-hours)and after app. 1 day (24-hours)	Length (mm)	Total liquid volume
1	Yellow	0-h: Yellow 24-h: Yellow	152 mm	0.4 ml
2	Orange	0-h: Orange 24-h: Orange	200 mm	0.6 ml
3	Clear	0-h: Blue (strong) 24-h: Clear	200 mm	4.8 ml
4	Orange	0-h: Orange 24-h: Orange	200 mm	0.4 ml
5	Pink	0-h: Pink (weak) 24-h: Pink	125 mm	0.4 ml
6	Yellow with red traces	0-h: Green (strong) 24-h: Green/yellow	122 mm	8 ml
7	Green/yellow	0-h: Yellow/green (weak) 24-h: Yellow/green	150 mm	3 ml
8	Yellow	0-h: Yellow (weak) 24-h: Yellow	40 mm	< 100 µl

Product no.	Colour before snapping	Colour immediately after snapping (0-hours)and after app. 1 day (24-hours)	Length (mm)	Total liquid volume
9	Green/yellow	0-h: Green 24-h: Green	203 mm	0.6 ml
10	Clear with yellow glow	0-h: Blue 24-h: Clear	295 mm	90 ml
11	Red	0-h: Red 24-h: Red	100 mm	5 ml
12	Yellow	0-h: Yellow 24-h: Yellow	40 mm	100 µl
13	Red	0-h: Pink 24-h: Red	198 mm	8.5 ml
14	Red	0-h: Red 24-h: Red	295 mm	20 ml
15	Orange	0-h: Orange 24-h: Orange	200 mm	0.6 ml

TABLE 6.4 COLOUR, MEASUREMENT AND LIQUID VOLUME OF GLOW STICKS FOR SCREENING ANALYSIS

6.4.2 Results of concentration of oxidizing agents

The concentration of oxidizing agents found in the outer tube of the glow stick during titration is stated in Table 6.5. The RSD % is the relative standard deviation calculated on the basis of the analyses in duplicate. The applied analysis is not specific as it analyses for all oxidizing agents, but with a starting point in the information that appeared in the survey it is anticipated that hydrogen peroxide is in question.

Product no.	Single analysis % H_2O_2	Average % H_2O_2	RSD %
1	0.41 0.3	0.40	5.3
2	0.37 0.38	0.37	1.9
3	1.10 1.12	1.11	1.2
4	0.97 0.96	0.96	1.0
5	0.90 0.89	0.89	0.66
6	2.21 2.15	2.18	1.9
7	0.90 0.87	0.88	2.4
9	2.29 2.42	2.36	4.0
10	2.06 2.08	2.07	0.51
11	1.23 1.24	1.24	0.49
13	1.03 1.07	1.05	2.4
14	2.08 2.08	2.08	0.05
15	1.26 1.28	1.27	1.2

TABLE 6.5 RESULTS OF CONCENTRATION OF OXIDIZING AGENTS IN GLOW STICKS

Two types of glow sticks (no. 8 and 12) had very small dimensions and correspondingly small liquid volumes which made it impossible to remove enough content to carry out the titration.

In all cases, the oxidizing agents were found in the clear liquid in the outer tube of the glow stick. Three products (no. 4, 11 and 12) were investigated to find out if the clear liquid contained water. A Karl-Fischer titration determined the water content to less than 1.5% for all three glow sticks. In addition, the liquids were investigated by GC-FID for content of alcohols. No alcohols were demonstrated in the clear liquid in the three glow sticks that were investigated.

The results show that the concentration of oxidizing agents (probably hydrogen peroxide) is between 0.4 and 2.4%. According to the table in Appendix 7, the manufacturers stated a content of between 0.5 and 1.2%.

6.4.3 Results of screening analysis of glow sticks

The screening analyses identified the solvents that were in concentrations exceeding 5%. From Table 6.4 it appears which colour of each type of glow stick was analysed.

In table 6.6 the identified solvents are compared with the solvents, which the manufacturers had given information about during the survey. There was agreement in two cases and in seven cases there were differences. In six cases there was no information (stated as ”not relevant”).

Product no.	Information about contents from manufacturers	Identified solutions via screening analysis	Agreement
1	85-95% Dimethyl phthalate	Tributyl citrate 1,2,3-propanetriol diacetate	No
2	90% Dimethyl O-phthalate	Dimethyl phthalate Tributyl acetyl citrate	No
3	22.5% Butyl benzoate 46% Dimethyl phthalate 22.5% Tributyl o-acetylcitrate	Butyl benzoate Dimethyl phthalate Tributyl acetyl citrate	Yes
4	None	Dimethyl phthalate Tributyl acetyl citrate	Not relevant
5	90-99% Dimethyl phthalate	Dimethyl phthalate	Yes
6	22.5% Butyl benzoate 46% Dimethyl phthalate 22.5% Tributyl o-acetylcitrate	Butyl benzoate Dimethyl phthalate Tributyl acetyl citrate	Yes
7	None	Dimethyl phthalate Tributyl acetyl citrate	Not relevant
8	None	Butyl benzoate Dimethyl phthalate	Not relevant
9	None	Dimethyl phthalate	Not relevant
10	30-40% Tributyl acetyl citrate	Dimethyl phthalate Tributyl acetyl citrate	No
11	50-70% Triethyl citrate	Dimethyl phthalate Tributyl acetyl citrate	No
12	50-70% Triethyl citrate	Dimethyl phthalate Triethyl citrate Tributyl acetyl citrate	No
13	50-70% Triethyl citrate	Dimethyl phthalate Tributyl acetyl citrate Triethyl citrate	No
14	50-70% Triethyl citrate	Dimethyl phthalate Tributyl acetyl citrate	No
15	None	Butyl benzoate Dimethyl phthalate Dibutyl phthalate	Not relevant

TABLE 6.6 RESULTS FROM GC-MS SCREENING OF GLOW STICKS

Based on the results of the screening analyses it was decided that the solvents in Table 6.7 should be quantified.

Name	CAS no.
Butyl benzoate	136-60-7
1,2,3-propanetriol diacetate	29860-16-0
Dibutyl phthalate	84-74-2
Dimethyl phthalate	131-11-3
Tributyl acetyl citrate	77-90-7
Tributyl citrate	77-94-1
Triethyl citrate	77-93-0

TABLE 6.7 SOLVENTS CHOSEN FOR QUANTIFICATION

6.4.4 Results of quantitative analyses

The results of the quantitative analyses for the chosen solvents are stated in Appendix 10 and the average of the results of the analyses in duplicate are shown in Table 6.8 where they are compared with the information about contents (obtained from the manufacturers during the survey).

Pro-duct no.	Information about contents from survey	Colour after snapping	Quantified substances	Amount of solvents
1	85-95% Dimethyl phthalate	Yellow	40% Tributyl citrate 56% 1,2,3-propanetriol diacetate	96%
2	90% Dimethyl-O-phthalate	Orange	49% Dimethyl phthalate 39% Tributyl acetyl citrate	88%
3	None	Blue	14% Butyl benzoate 49% Dimethyl phthalate 20% Tributyl acetyl citrate	83%
4	None	Orange	83% Dimethyl phthalate 21% Tributyl acetyl citrate	104%
5	90-99% Dimethyl phthalate	Pink	83% Dimethyl phthalate	83%
6	22.5% Butyl benzoate 46% Dimethyl phthalate 22.5% Tributyl acetyl citrate	Blue[1)] Green[1)]	17% Butyl benzoate 43% Dimethyl phthalate 26% Tributyl acetyl citrate	86%
7	None	Light blue	67% Dimethyl phthalate 15% Tributyl acetyl citrate	82%
8a[2)]	None	Yellow	17% Butyl benzoate 56% Dimethyl phthalate 16% Dibutyl phthalate	89 %
8b[2)]	None	Yellow	30% Butyl benzoate 56% Dimethyl phthalate	86%

Pro-duct no.	Information about contents from survey	Colour after snapping	Quantified substances	Amount of solvents
			0% Dibutyl phthalate	
9	None	Green	79% Dimethyl phthalate	79%
10	30-40% Tributyl acetyl citrate	Blue	58% Dimethyl phthalate 11% Tributyl acetyl citrate	69%
11	50-70% Triethyl citrate	Light blue[2)]	87% Dimethyl phthalate 18% Tributyl acetyl citrate	105%
12	50-70% Triethyl citrate	Yellow	35% Dimethyl phthalate 55% Triethyl citrate 16% Tributyl acetyl citrate	106%[3)]
13	50-70% Triethyl citrate	Light blue	38% Dimethyl phthalate 13% Tributyl acetyl citrate 40% Triethyl citrate	91%
14	50-70% Triethyl citrate	Green	67% Dimethyl phthalate 13% Tributyl acetyl citrate	80%
15	None	Orange	4% Butyl benzoate 30% Dimethyl phthalate 45% Dibutyl phthalate	79%

TABLE 6.8 RESULTS OF QUANTITATIVE ANALYSES

Notes to Table 6.8:
All glow sticks with blue colour had no colour before snapping. The other glow sticks had a pale shade of the colour they obtained after snapping. Results greater than 100% are due to the analysis uncertainty of the method of app. 11%. As there is a content of hydrogen peroxide, dye and phenyl oxalate esters, e.g. CPPO, it must be expected that the solvents amount to app. 99%.

1) Two different colours were analysed as two were not available in the same colour. Within the analysis uncertainty of the method the same concentration of solvents was demonstrated in the two glow sticks.
2) For product no. 8, different solvents were demonstrated in various examples of the same type of glow stick, during screening as well as during the quantitative analyses.
3) 24 hours after snapping, the two glow sticks had different colours (clear and light yellow, respectively). Within the measuring uncertainty of the method, the same concentration of solvents was demonstrated in the two glow sticks.

6.5 Comparison of results of chemical analyses

Investigations of the purchased glow sticks demonstrated that the liquid volume differed a lot; from less than 100 µl in the smallest glow sticks to app. 90 ml in the largest glow sticks.

The following solvents were demonstrated in the glow sticks:

- Butyl benzoate
- 1,2,3-propantriol diacetate
- Dibutyl phthalate
- Dimethyl phthalate
- Tributyl acetyl citrate

- Tributyl citrate
- Triethyl citrate.

The analyses show that the solvents constitute between 69% and 99% of the content in glow sticks.

The content of hydrogen peroxide was between 0.4 and 2.4% in the investigated glow sticks. In all cases, hydrogen peroxide existed in the clear liquid in the outer tube of the glow stick.

In connection with six of the glow sticks (product no. 3, 4, 7, 8, 9 and 15), there was no information on their content from the survey. In seven (product no. 1, 2, 10, 11, 12, 13 and 14) out of nine, where information existed, the information from the survey did not correspond with the identified solvents from the chemical analyses.

According to the survey, glow sticks no. 10-14 come from the same manufacturer, but they were purchased in two different online stores. The results show that the same manufacturer can use different solvents depending on which type of glow stick is being sold.

When analysing glow stick product no. 8 (mouth cover with yellow light), different solvents were demonstrated in the different versions of the product. That might be because the purchased products were manufactured on two different dates which cannot be traced via the packaging.

In connection with glow stick product no. 6, 7, 11, 13 and 14, different colours were analysed during the screening analyses and the quantitative analyses. Only in one case (product no. 13), a difference was found in the concentration of each solvent used in connection with different colours as the screening indicated a much higher content of dimethyl phthalate and a lower content of triethyl citrate than demonstrated during the quantitative analyses.

On the label of glow stick product no. 2, a content of i.a. dimethyl phthalate, tributyl citrate and tributyl acetyl citrate was stated, but only dimethyl phthalate and tributyl acetyl citrate were demonstrated. The package contains several colours so it cannot be excluded that other colours contain tributyl citrate.

7. Discussion

7.1 Comparison of analysis results and expected content

Analyses of the chosen constituents of glow sticks show that 69 – 99% of the contents are composed of the solvents that were analysed for. Including the oxidizing agents (hydrogen peroxide) the analysis in total accounted for minimum 70% of the chemical substances in glow sticks and in most cases more than 99% of the content.

The final per cents are composed by the dye (app. 0.1%), one or several phenyl oxalate esters, e.g. CPPO (1 – 13.5%) and 2-methyl-propane-2-ol (< 10%), assessed on the basis of information that appeared during the survey, see Appendix 7.

During the survey, information was collected about expected contents in nine of the 15 analysed products. When comparing the information with the results of the chemical analyses, the information is only roughly correct for two of the glow stick products. In the other glow stick products, considerable amounts were identified of substance that had not been informed and/or the concentration of one or more deviated substantially.

Contents were stated on the packaging of one of the glow stick products and they had been confirmed during the chemical analyses. The stated contents did not correspond with the information collected during the survey.

Information on the concentration of hydrogen peroxide appeared during the survey and did not differ decisively from the found concentrations.

7.2 Classification of health risk

In 2013, the European Chemicals Agency (ECHA) made a decision on which type of product, glow sticks should belong to and which legislation the products should follow, see paragraph 1.4. As the product is defined as a chemical mixture used for personal ornamentation and gimmicks and gags it must not contain substances or mixtures that must be classified as hazardous.

In so far the substances do not have a harmonised classification, the manufacturer must self-classify. That makes it possible to have different classifications of a substance, depending on the data used, interpretation of data etc.

The analysed products demonstrated a substantial content of triethyl citrate, tributyl citrate, tributyl acetyl citrate and 1,2,3-propantriol diacetate in several of the products. The substances are not classified and do not constitute any known health risks. Appendix 8 gives an outline of the found classification and health effects of the found substances related to the concentrations in the glow stick products that were surveyed.

14 of the analysed products contained dimethyl phthalate. To which degree these 14 products are legal according to REACH depends on the self-classification of dimethyl phthalate.

The most frequently used self-classification for dimethyl phthalate in ECHA's database is currently "not classified". On the basis of information available on Toxnet in the Hazardous Substances Data Base[25] this classification seems doubtful as it is well-described that dimethyl phthalate gives reversible eye irritation, burning sensations in throat and stomach when ingested and lethargy from swallowing larger doses (effect on the central nervous system).

Among the analysed products for which a safety data sheet has been forwarded, dimethyl phthalate is not classified as dangerous in accordance with the EU regulations.

One product contained dibutyl phthalate that figures on the EU list of dangerous substances. The substance has been included on the approval scheme and application must be approved before 21.02.2015. Dibutyl phthalate has a harmonised classification as reproduction toxic in category 1B (Rep 1B) with H360Df: "May damage fertility or the unborn child". The concentration limit for when a mixture containing this substance must be classified as reproduction toxic is 0.3%. The substance must not be used without special permission.

According to the order on prohibition of phthalates in toys and articles for younger children[26], dibutyl phthalate has been forbidden in products for children of up to 3 years of age since 2009 (limit value 0.05%). According to the Reach Regulation, it has since 16 January 2007 been forbidden to make and import toys and articles for children of up to 14 years that contain dibutyl phthalate (limit value 0.1%).

That means that the use of dibutyl phthalate in glow sticks, considered to be toys, is a violation of the law.

Five of the products contain butyl benzoate which in ECHA's database most frequently is self-classified as "Skin irritating 2" and "Eye irritating 2". The glow stick manufacturers who have forwarded safety data sheets have all classified butyl benzoate as "not dangerous". If butyl benzoate is classified as dangerous, then four of the glow stick mixtures will for that reason have to be classified as dangerous.

If dimethyl phthalate and butyl benzoate are classified as health hazardous and assessed to constitute a health risk, then according to REACH only one product (product no. 1) of the 15 analysed products is legal as a gimmick and gag product.

Hydrogen peroxide was not demonstrated in concentrations that involved the classification and labelling of the product.

None of the suppliers who submitted safety data sheets classified the glow stick liquid as dangerous.

7.3 Health hazardous effects

Only a few of the citizens who contacted poison centres and casualty wards after having been in contact with the contents of glow stick products had symptoms, see paragraph 3.1. Of the registered symptoms, stinging sensations and unpleasantness in mouth and throat after oral digestion amounted to app. 85%.

Acute health effects after contact with the content in glow sticks may especially be due to two substances and they are dimethyl phthalate and butyl benzoate which both often appear in substantial amounts in the products. Dimethyl phthalate was found in 14 of the 15 analysed products. Butyl benzoate appeared in five products.

Hydrogen peroxide appeared in low concentrations and is expected to react with other chemicals immediately when the glow stick is punctured. It is hardly expected that the substance would lead to perceivable acute effects during accidents.

[25] http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
[26] https://www.retsinformation.dk/Forms/R0710.aspx?id=126137

Through the analyses, a volume of the glow stick products was registered and it varies from less than 100 µl in the smallest glow sticks to app. 90 ml in the largest glow sticks.

Acute effects of dimethyl phthalate and butyl benzoate especially occur after swallowing or contact with the eyes.

The consequence of oral intake will of course depend on the amount of substance. Glow sticks with a large liquid volume will give severe unpleasantness when the entire amount is swallowed if it contains dimethyl phthalate or butyl benzoate. In contact with moist mucous membranes, the substances will give rise to a stinging sensation from throat to stomach. Due to the acute effect it is less probable that the large glow stick products will be completely emptied and swallowed.

When in contact with the eyes the volume of the glow stick does not have the same significance, as only a limited amount can come into contact with the eyes. However, the liquid volume in the glow stick is of importance to the risk of splashes hitting the eye when the glow stick is punctured.

The effects that are expected due to the identified substances and their concentrations correspond to the symptoms reported at poison centres etc. as described in paragraph 3.1.

Butyl benzoate can have a skin irritating effect and could be the reason for the reported cases of irritated skin, see paragraph 3.1.

If dimethyl phthalate and butyl benzoate were not used in glow sticks, the acute effects observed after contact with the content would most likely be reduced significantly. However, the number of inquiries to casualty wards, poison centres etc. that are due to worries about children who have no symptoms, would probably remain unaffected.

The occurrence of dibutyl phthalate in glow sticks is not expected to have any acute effects. The prohibition of dibutyl phthalate addresses a risk of hormone-like effects in unborn children and a risk of reduced fertility among adults. After one single exposure, the risk of these effects is presumably very limited.

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Appendix 1: Survey - General inquiry to companies that were regarded as possible distributors of glow stick products

Inquiry about glow products for children

On behalf of the Danish Environmental Protection Agency, Danish Technological Institute is carrying out a survey of the Danish market for glow stick products, especially products that are aimed at children aged up to 14 years.

In that connection, we would like to know if your company sells glow sticks to children, and if so which products are in question.

Glow sticks are disposable and require neither power source nor light to give off light. Glow sticks contain two isolated chemicals. When the stick is snapped, the two chemicals are mixed and a fluorescent (luminescent) solution is created. The glow sticks may come in various shapes, e.g. glasses, bracelets, caps or sticks.

For clarity reasons we have gathered the questions in the enclosed questionnaire, which we hope you will find time to fill in.

Unfortunately, we have a very tight time schedule and would therefore appreciate to receive your response by XXday XX 2012.

For the sake of good order we would like to mention that Danish Technological Institute is bound by professional secrecy and therefore respects the confidentiality of any company-specific information you may give us.

If you have any questions in connection with the above or the questionnaire, then please do not hesitate to contact us.

Best regards
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Kathe Tønning, tel. +45 72 20 18 30, e-mail krt@teknologisk.dk

The questions exclusively relate to <u>glow stick products aimed at children</u>

Question	Yes	No
Does your company sell glow stick products for children (e.g. glasses, bracelets, caps etc.)?		
If yes, then please state which products:		

Question	Yes	No
Do glow stick products for children form part of your fixed product range?		
If no, do they periodically form part of your product range?		
If yes, which periods?		

If your company sells glow stick products aimed at children, then please answer the following.

Question	Yes	No
Do you have any written information about the composition and content of the glow stick products (e.g. safety data sheets, information from suppliers/manufacturers or others)?		
If yes, then please submit a copy of the information together with the completed questionnaire.		

Please specify supplier, importer and/or manufacturer

Comments

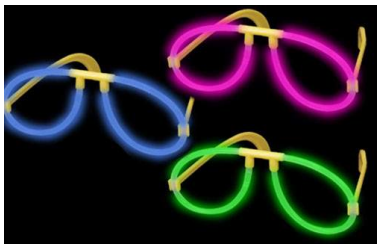
Appendix 2: Survey - Inquiry to companies whose products were registered in retail shops

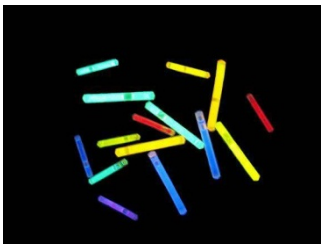
Inquiry about glow stick products for children

On behalf of the Danish Environmental Protection Agency, Danish Technological Institute is carrying out a survey of the Danish market for glow stick products, especially products which are aimed at children aged up to 14 years.

During our survey we have in your shop come across products directed at children.

Glow sticks are disposable and require neither power source nor light to give off light. Glow sticks contain two isolated chemicals. When the stick is snapped, the two chemicals are mixed and a fluorescent (luminescent) solution is created. The glow sticks may come in various shapes, e.g. glasses, bracelets, caps or sticks.





As part of the survey, we would like to ask you some questions about the products. For clarity reasons, we have gathered the questions in the enclosed questionnaire, which we hope you will find time to fill in.

Unfortunately, we have a very tight time schedule and would therefore appreciate to receive your response by XXday XX 2012.

For the sake of good order we would like to mention that Danish Technological Institute is bound by professional secrecy and therefore respects the confidentiality of any company-specific information you may give us.

If you have any questions in connection with the above or the questionnaire, then please do not hesitate to contact us.

Best regards
Eva Jacobsen, tel. +45 72 20 18 93, e-mail evj@teknologisk.dk
Kathe Tønning, tel. +45 72 20 18 30, e-mail krt@teknologisk.dk

The questions exclusively relate to <u>glow stick products aimed at children</u>
Shop

Question	Yes	No
Do glow stick products for children form part of your fixed product range?		
If no, do they then periodically form part of your product range?		
If yes, which periods?		

If your company sells glow stick products aimed at children, then please answer the following questions.

Question	Yes	No
Do you have any written information about the composition and content of the glow stick products (e.g. safety data sheets, information from suppliers/manufacturers or others)?		
If yes, then please submit a copy of the information together with the completed questionnaire.		

Please specify supplier, importer and/or manufacturer
Comments

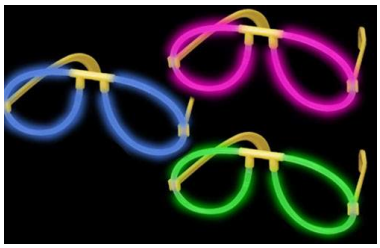
Appendix 3: Survey – Inquiry to online stores where the survey demonstrated sale of products aimed at children or that could appeal to children

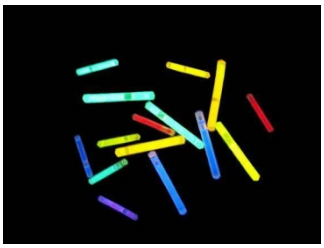
Inquiry about glow products for children

On behalf of the Danish Environmental Protection Agency, Danish Technological Institute is carrying out a survey of the Danish market for glow stick products, especially products that are aimed at children aged up to 14 years.

During our survey, we have in your online shop come across products aimed at children.

Glow sticks are disposable and require neither power source nor light to give off light. Glow sticks contain two isolated chemicals. When the stick is snapped, the two chemicals are mixed and a fluorescent (luminescent) solution is created. The glow sticks may come in various shapes, e.g. glasses, bracelets, caps or sticks.





In connection with this survey, we would like to ask you some questions about the products. For clarity reasons we have gathered the questions in a questionnaire, which we hope you will find time to fill in.

Unfortunately, we have a very tight time schedule and would therefore appreciate to receive your response by XXday XX 2012.

For the sake of good order, we would like to mention that Danish Technological Institute is bound by professional secrecy and therefore respects the confidentiality of any company-specific information you may give us.

If you have any questions in connection with the above or the questionnaire, then please do not hesitate to contact us.

Best regards
Eva Jacobsen, tel. +45 72 20 18 93, e-mail evj@teknologisk.dk
Kathe Tønning, tel. +45 72 20 18 30, e-mail krt@teknologisk.dk

The questions exclusively relate to <u>glow stick products aimed at children</u>
Shop

Question	Yes	No
Do glow stick products for children form part of your fixed product range?		
If no, do they periodically form part of your product range?		
If yes, which periods?		

If your company sells glow stick products aimed at children, then please answer the following questions.

Question	Yes	No
Do you have any written information about the composition and content of the glow stick products (e.g. in the form of safety data sheets, information from suppliers/manufacturers or others)?		
If yes, then please submit a copy of the information together with the completed questionnaire.		

Please specify supplier, importer and/or manufacturer
Comments

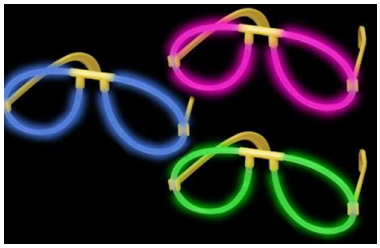
Appendix 4: Survey – Inquiry to manufacturers/importers

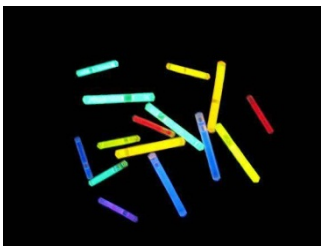
Inquiry about glow products for children

On behalf of the Danish Environmental Protection Agency, Danish Technological Institute is carrying out a survey of the Danish market for glow stick products, especially products that are aimed at children aged up to 14 years.

During our survey we have come across products manufactured/imported by you.

Glow sticks are disposable and require no power source or light to give off light. Glow sticks contain two isolated chemicals. When the stick is snapped, the two chemicals are mixed and a fluorescent (luminescent) solution is created. The glow sticks may come in various shapes, e.g. glasses, bracelets, caps or sticks.





As part of the survey, we would like to ask you some questions about the products. For clarity reasons we have gathered the questions in a questionnaire, which we hope you will find time to fill in.

Unfortunately, we have a very tight time schedule and would therefore appreciate to receive your response by XXday XX 2012.

For the sake of good order, we would like to mention that Danish Technological Institute is bound by professional secrecy and therefore respects the confidentiality of any company-specific information you may give us.

If you have any questions in connection with the above or the questionnaire, then please do not hesitate to contact us.

Best regards
Eva Jacobsen, tel. +45 72 20 18 93, e-mail evj@teknologisk.dk
Kathe Tønning, tel. +45 72 20 18 30, e-mail krt@teknologisk.dk

The questions exclusively relate to <u>glow stick products aimed at children</u>

Manufacturer/importer

Question	Yes	No
Do glow stick products form part of your fixed product range?		
If no, do they periodically form part of your product range?		
If yes, which periods?		

Question	Yes	No
Do you have any written information about the composition and content of the glow stick products (e.g. safety data sheets, information from suppliers/manufacturers or others)?		
If yes, then please submit a copy of the information together with the completed questionnaire.		

Comments

Appendix 5: Survey – Result of inquiries

Manufacturers/importers/distributors of the glow stick products (registered when visiting shops and via internet pages) were contacted. Contact consisted of an informative letter and a questionnaire (see appendix 1, 2, 3 and 4).

Four types of inquiries were in question:

- General inquiry to companies that were regarded as possible distributors of glow stick products (see Appendix 1).
- Inquiry to companies whose products were registered in retail shops (see Appendix 2).
  Inquiry was prepared in Danish and English.
- Inquiry to online stores where the survey demonstrated a sale of products aimed at children or that could appeal to children (see Appendix 3).
- Inquiry to manufacturers and importers (see Appendix 4).
  Inquiry was prepared in Danish and English.

The results of the inquiries appear from the tables below.

Result of general inquiries to companies that were regarded as possible distributors of glow stick products.
27 companies were contacted and replies were received from 26 companies.

Question	Yes	No
Does your company sell glow stick products to children (e.g. glasses, bracelets, caps, etc.)?	7	19

Result of inquiries to companies whose products were registered in retail shops.
A total of four shops were contacted and replies were received from two shops.

Question	Yes	No
Do glow stick products for children form part of your fixed product range?	1	1
If no, do they periodically form part of your product range?	1	

Result of inquiry to online stores where the survey demonstrated a sale of products that were aimed at children or that could appeal to children.
A total of 28 internet stores were contacted and replies were received from nine stores.

Question	Yes	No
Do glow stick products for children form part of your fixed product range?	3	6
If no, do they periodically form part of your product range?	2	3

Result of inquiry to manufacturers and importers.
10 manufacturers/importers were contacted and replies were received from five.

Question	Yes	No
Do glow stick products for children form part of your fixed product range?	4	1
If no, do they periodically form part of your product range?	1	

Appendix 6: Survey – Inquiry to Danish chain shops

In the project, a general inquiry was sent to a number of Danish chain shops.
The following shops are concerned:

- Coop Danmark A/S
- Dansk Supermarked A/S
- JYSK A/S
- Tiger
- Imerco
- Magasin
- Søstrene Grenes Import A/S
- GK Legetøj ApS (Buddy Legetøj)
- Legekæden A.M.B.A
- Fætter BR
- TOP-TOY A/S (Toys'R'us)
- jem & fix A/S
- SILVAN
- Bygma A/S
- A/S Harald Nyborg
- XL-byg
- Stark
- K E Mathiasen Legetøj A/S
- Aldi
- Kiwi Danmark A/S
- Spar Danmark A/S
- Kop & Kande
- T. Hansen
- Bahne
- Maki A/S
- Sportmaster
- INTERSPORT Danmark A/S.

Appendix 7: Result of inquiry on composition and contents

The following tables give a total outline of the result of the inquiry on composition and content sent to manufacturers/importers/distributors during the survey.

The two tables are grouped according to how their classification was estimated in relation to this project.

CAS no.	Name	Concentration %
136-60-7	Butyl benzoate	0-45
77-90-7	Tributyl acetyl citrate	0-40
77-93-0	Triethyl citrate	0-70
75-65-0	2-methyl-2-propanol(Tert-butyl-alcohol)	0-10
7722-84-1	Hydrogen peroxide	0.05-1.2%
75203-51-9	CPPO	1-13.5
131-11-3	Dimethyl phthalate (DMP)	0-99
30431-54-0	CPPO: Bis[3,4,6-trichloro-2-(pentyloxycarbonyl)phenyl] oxalate	0-13.5
75203-51-9	bis[2,3,5-trichloro-6-(pentyloxycarbonyl)phenyl] oxalate	4.95
110904-87-5	BPEN (Blue)	0.05-0.8

TABLE 1 SUBSTANCE REGISTERED AS HAVING EITHER HARMONISED CLASSIFICATION OR SELF-CLASSIFICATION.

CAS no.	Name	Colour	Concentration %
54-21-7	Sodium salicylate		0-0.005
128-37-0	2,6-di-tert-butyl-p-Cresol		0-0.015
1499-10-1	9,10-diphenyl anthracene	Purple	0.1
10075-85-1	9,10-bis(phenylethynyl)-anthraceneBPEA	Green	0.1
41105-35-5	1-chloro-9,10-bis(phenylethynyl)-anthracene	Yellow	0.1
112100-07-9	1,6,7,12,TETRAPHENOXY-N-N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylenedicarbamide	Red	0.1
51749-83-8	1,8-Dichloro-9,10-bis(phenylethynyl)anthracene	Yellow	0.01
335654-34-7	1,6,7,12-tetra(p-t-butylphenoxy)-N-N´-dibutyl3,4,9,10-perylenedicarboximide	Red	0.01
112100-07-9	N,M--dibutyl-5,6,12,113-tetraksis(4-(1,1-dimethylethyl)Phenoxy)-3,4,9,10-perylendicarboximide	Red	0.08

TABLE 2 SUBSTANCE CONTENTS THAT ARE EXPECTED TO CONSTITUTE MAX. 0.1 % AND WHERE IT HAS BEEN INVESTIGATED IF CLASSIFICATION EXISTS

Appendix 8: Outline of health effects of contents in glow sticks

The below table states substances in glow sticks that were informed by the manufacturer or that were identified during analyses.

”Concentration” means the concentration of chemical substances (weight %) found when analyzing the glow sticks.

”Health effect” is the health effect of the pure substance as stated in various sources.

”Health effects of glow sticks” means the expected health effect of glow sticks e.g. at the concentrations that can be expected from the analyses.

”H sentences”: H302 Harmful if swallowed; H312 Harmful in contact with skin; H315 Causes skin irritation; H319 Causes serious eye irritation; H332 Harmful if inhaled; H335 May cause respiratory irritation; H360Df May damage fertility of the unborn child.

Name	CAS no.	Concen-tration Weight %	Health effects	Health effects of glow sticks	H sentence
Sodium salicylate	54-21-7	-	Causes eye irritation, harmful if swallowed	Poor	H302, H319
2-methyl-2-propanol(Tert-butyl-alcohol)	75-65-0	-	Causes eye irritation	Poor	H319, H332, H335
Butyl citrate	77-94-1	0 - 57	None	None	None
Tributyl acetyl citrate	77-90-7	0 - 31	None	None	None
Triethyl citrate	77-93-0	0	Skin, eye and stomach irritation	Not demonstrated	None
Dibutyl phthalate (DBP)	84-74-2	0 - 55	May harm the unborn child and damage fertility	Poor, but undesirable	H360Df
2,6-di-tert-butyl-p-Cresol	128-37-0	-	None	None	None
Dimethyl phthalate (DMP)	131-11-3	0 - 94	Eye and respiratory irritation, CNS-effect	Obvious	None
Butyl benzoate	136-60-7	0 - 53	Skin, eye and stomach irritation	Obvious	H315, H319
Hydrogen peroxide	7722-84-1	0.4 – 2.4	Eye irritation	Poor	H319 at 5 - 8%

Name	CAS no.	Concen-tration Weight %	Health effects	Health effects of glow sticks	H sentence
Glycerol diacetate	25395-31-7	0 - 38	None	None	None
CPPO: Bis(3,4,6-trichloro-2-carbo-pentoxy phenyl) oxalate	30431-54-0	-	Unknown	Unknown	H302, H312, H332
CPPO: Bis[3,4,6-trichloro-2-(pentyloxy carbonyl)phenyl] oxalate	75203-51-9	-	Unknown	Unknown	

Appendix 9: Labelling of packaging from glow sticks

Product no.	Product type	CE marked	Not recom-mended for age	Text on packaging or in the enclosed directions	Text in Danish
1	Mask	Yes	0-3	Before using, bend the glow sticks at several places. Do not cut or prick the glow sticks. May cause permanent stains on clothing and furniture. Avoid contact with eyes and skin. In case of contact with eyes or skin rinse thoroughly with water. Do not drink or swallow the contents. Do not expose the glow sticks to direct sunlight or hot temperature. After use, the glow stick needs to be disposed of.	Yes
2	Bracelet	Yes	0-3	Do not drink the liquid. In case of leakage avoid contact with eyes and clothes. Rinse immediately with water. Dimethyl phthalate, tert-butyl alcohol, BHT, hydrogen peroxide, natrium salicylate, water, tributyl acetyl, tributyl acetyl citrate, CPPO and specification of dyes.	Yes
3	Stick	No	Child's head shown	Not for children! Only for decoration purposes! Leave the rod in its original packaging until use. Do not expose to direct sunlight. Do not damage or cut up the plastic jacket. Contact with skin, eyes or mucus membranes may result in irritation. Rinse out carefully and contact a doctor. Do not eat or swallow the component or contents! SUFFOCATION RISK!	Yes
4	Bracelet	Yes	0-3	Do not puncture or cut plastic tubes. Ingredients are non-flammable and non-toxic but may permanently stain clothing or furniture. Contact with skin or eyes may cause temporary discomfort. In case of skin or eye contact, rinse thoroughly with water. Do not drink or ingest contents. Do not leave glow sticks in direct sunlight or expose to high temperatures. After use, dispose of in refuse container.	No

Product no.	Product type	CE marked	Not recom-mended for age	Text on packaging or in the enclosed directions	Text in Danish
5	Earrings	Yes	0-4	Do not drink the fluid in the lights. The fluid is not hazardous, but may cause irritation of the eyes. Flush thoroughly with clean water if the contents come into contact with the eyes. Do not bend the tubes with too much force as this may perforate them and cause the contents to escape. The packaging should be used for storage of the remaining lights and to keep the warnings and instructions for use.	Yes
6	Stick	Yes	0-5	Only to be used under the supervision of adults. Do not expose to high tempera-tures or leave glow sticks in direct sun-light. Do not cut or puncture the plastic tube. Do not snap the product after it has been activated. The contents are non-toxic and non-flammable, but may stain furniture or clothes permanently. Contact with skin or eyes may cause temporary discomfort. Rinse thoroughly with water. Do not drink the contents.	Yes
7	Stick	Yes	0-3	Do not puncture or cut plastic tubes. Contact with skin or eyes may cause temporary discomfort. In case of skin or eye contact, rinse thoroughly with water. Do not drink or ingest contents. Do not leave glow sticks in direct sunlight or expose to high temperatures. After use, dispose product.	No
8	Mouth cover	Yes	0-5	Keep product in original package until ready to use. Do not puncture or cut plastic tube. Ingredients are non-toxic and non-flammable, but may permanently stain furniture or clothing. Contact with skin or eyes may cause temporary discomfort. In case of skin or eye contact, rinse thoroughly with water. Do not drink or ingest contents. Do not leave lightstick in direct sunlight or expose to high temperatures. After use, dispose of in refuse container.	No

Product no.	Product type	CE marked	Not recom-mended for age	Text on packaging or in the enclosed directions	Text in Danish
9	Glasses	Yes	0-3	Do not damage or cut plastic tubes at any time. Ingredients are non-flammable but may stain furniture or clothing permanently. Contact with skin or eyes may cause discomfort. If contact occurs, rinse thoroughly with water. Do not drink or ingest contents. Do not expose lightsticks to direct sunlight or high temperature. Do not bend after activation. After use, dispose of in refuse container.	No
10	Giant rod	No	0-5	Keep product in original packaging until ready to use. Do not cut or puncture plastic tube. Do not bend product a second time after activation. Contents of tube are non-toxic and non-flammable, but may stain furniture and clothing permanently. Skin or eye contact may cause temporary discomfort. Rinse thoroughly with water. Do not drink or ingest contents. Do not expose product to high temperatures or direct sunlight.	No
11	Whistle	Yes	0-3	Keep product in original bag until ready to use. Do not puncture or cut plastic tubes. Ingredients are non-flammable and non-toxic, but may permanently stain clothing or furniture. Contact with skin or eyes may cause temporary dis-comfort. In case of skin or eye contact, rinse thoroughly with water. Do not drink or ingest contents. Do not leave glow sticks in direct sunlight or expose to high temperatures. After use dispose of in refuse container.	No
12	Straw	Yes	0-3	Keep product in original bag until ready to use. Do not puncture or cut plastic tubes. Ingredients are non-flammable and non-toxic, but may permanently stain clothing or furniture. Contact with skin or eyes may cause temporary dis-comfort. In case of skin or eye contact, rinse thoroughly with water. Do not drink or ingest contents. Do not leave glow sticks in direct sunlight or expose to high temperatures. After use dispose of in refuse container.	No

Product no.	Product type	CE marked	Not recom-mended for age	Text on packaging or in the enclosed directions	Text in Danish
13	Clapping hand	Yes	0-3	Non-toxic and non-flammable. Contact with eyes or skin may cause temporary discomfort – rinse with water. Do not drink or ingest contents. Do not leave glow sticks in direct sunlight or expose to high temperatures.	No
14	Sticks	Yes	0-5	Keep product in original bag until ready to use. Do not puncture or cut plastic tubes. Ingredients are non-flammable and non-toxic, but may permanently stain clothing or furniture. Contact with skin or eyes may cause temporary dis-comfort. In case of skin or eye contact, rinse thoroughly with water. Do not drink or ingest contents. Do not leave glow sticks in direct sunlight or expose to high temperatures. After use dispose of in refuse container.	No
15	Bracelet	No	Not stated	No text	No

Appendix 10: Results of chemical analyses of glow sticks

The below tables state the individual analysis results grouped according to the name of the substances. RSD is the relative standard deviation calculated for the analysis in duplicate.

Product no.	Concentration (%)	Average conc. (%)	RSD (%)
3	13	14	15
	16		
6	16	17	4
	17		
8a	17	24	38
8b	30		
15	4.1	4.1	0.4
	4.1		

TABLE 1 BUTYL BENZOATE, CAS NO. 136-60-7

Product no.	Concentration (%)	Average conc. (%)	RSD (%)
1	58	56	4
	55		

TABLE 2 1,2,3-PROPANTRIOL DIACETATE, CAS NO. 29860-16-0

Product no.	Concentration (%)	Average conc. (%)	RSD (%)
8a	16	7.8	
8b	i.p.		
15	45	45	2
	44		

TABLE 3 DIBUTYL PHTHALATE, CAS NO. 84-74-2

Product no.	Concentration (%)	Average conc. (%)	RSD (%)
2	50	49	3
	48		
3	50	49	3
	48		
4	78	83	8
	88		
5	84	83	1
	82		
6	43	43	1
	44		
7	66	67	3
	69		
8	55	56	0.8
	56		
9	82	79	4
	77		
10	60	58	4
	57		
11	84	87	5
	90		
12	35	35	2
	36		
13	39	38	3
	37		
14	66	67	4
	69		
15	29	30	4
	30		

TABLE 4 DIMETHYL PHTHALATE, CAS NO. 131-11-3

Product no.	Concentration (%)	Average conc. (%)	RSD (%)
2	38	39	4
	40		
3	19	20	8
	21		
4	24	21	25
	17		
6	27	26	6
	24		
7	15	15	4
	16		
10	11	11	4
	11		
11	18	18	1
	17		
12	15	16	6
	17		
13	12	13	0.4
	13		
14	13	13	7
	12		

TABLE 5 TRIBUTYL ACETYL CITRATE, CAS NO. 77-90-7

Product no.	Concentration (%)	Average conc. (%)	RSD (%)
1	36	40	16
	45		

TABLE 6 TRIBUTYL CITRATE, CAS NO.77-94-1

Product no.	Concentration (%)	Average conc. (%)	RSD (%)
12	52	55	9
	59		
13	39	40	2
	41		

TABLE 7 TRIBUTYL CITRATE, CAS NO.77-93-0

Survey and health assessment of glow sticks

The project ”Survey and health assessment of glow sticks” was carried out from July 2012 till May 2013. This report describes the project results, including a survey, chemical analyses of selected substances in the glow stick liquids and an assessment of the exposure and health hazards for the consumer.

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Environmental Protection Agency

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