

Survey of white spirit

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Survey of white spirit

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Preface

Background and objectives

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2010a) includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic based on quantitative structure analogy relationship evaluation using computer models using computer models, or otherwise been of concern or in political focus. For inclusion in the list, substances in general must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, and information regarding on-going activities under REACH, among others.

The main objective of this survey is to provide background for the Danish EPA's consideration regarding the need for further risk management measures. On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns 3 oil-derived substances termed as *white spirits* with the CAS numbers: 64742-88-7; 64742-82-1; 8052-41-3. The reasons for including these substances on LOUS are that they have special focus in Denmark because of their potential for chronic effects on the central nervous system (the "painter's syndrome") after long term inhalation exposure. Furthermore, the substances have to be classified as carcinogenic in category 1B if the content of benzene in the substances is not controlled down to a level below 0.1 %.

The process

The survey has been undertaken by DHI, Denmark, from March to June 2013.

The project participants were:

- Poul Bo Larsen, DHI, project manager
- Anja Kamper, DHI, contributor
- Henrik Rye Lam, DHI, quality supervisor

The work has been followed by an advisory group consisting of:

- Lea Stine Tobiassen, Danish EPA, Chair of advisory group
- Christina Ihlemann, Danish EPA
- Kathrine Smidt, Danish EPA
- Anna-Louise Jørgensen Rønlev, Danish EPA (Århus)

- Birgitte Marcussen, The Danish Society for Nature Conservation
- Anette Harbo Dahl, Danmarks Farve og Limindustri
- Nanna Vind, Danish Working Environment Authority
- Ulla Telcs, Confederation of Danish Industry
- Helle Fabiansen, Plastindustrien
- Michael Mücke Jensen, Energi og Olieforum

Data collection

This survey/review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors as indicated further below.

The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower) and the German Angel.
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Date on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet)
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA) and the INIRIS database.
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
 - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
 - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvarsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature.
 - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
- PubMed and Toxnet databases for identification of relevant scientific literature.

This survey is mainly based on a compilation of existing reports and evaluations that has been made over time including data from the REACH system and from the common Nordic product register database, SPIN.

In addition to the written literature the following persons besides the advisory group members have contributed with valuable information/ advice:

Mogens Kragh Hansen, Arbejdsmiljøhuset Sigurd Mikkelsen, Bispebjerg Hospital Erik Pedersen, Nord (previous Kommunekemi) Thomas Mathiesen, Estichem

Summary and conclusions

This survey concerns 3 oil-derived hydrocarbon substances termed as *white spirits* (mineral turpentine). The reasons for including these substances on LOUS are that they have special focus in Denmark because of their potential for chronic effects on the central nervous system (the "painter's syndrome") after long term occupational inhalation exposure.

The main objective of this survey is to provide background for the Danish EPA's consideration regarding the need for further possible risk management measures.

Identification and physical-chemical properties of the substances

The white spirits in question are all hydrocarbon solvents defined as UVCB substances (i.e. substances of Unknown or Variable composition, Complex reaction products or Biological materials) with a high content of aromatic hydrocarbons (i.e. 15-20%).

All three substances are oil derived substances and the exact chemical content is dependent on the quality of the raw oil and the refinery processes to which they have been subjected. Based on their definition they are not chemically distinguishable from each other as they have similar and overlapping hydrocarbon composition.

The three substances are:

- a) white spirit type 0 (CAS 64742-88-7)
- b) white spirit type 1 (CAS 64742-82-1)
- c) Stoddard solvent (CAS 8052-41-3)

White spirit type 1 is the European counterpart of Stoddard solvent (US term of the substance) and is the most widely used white spirit with high aromatic content in Europe.

Overall the content of the three substances can be described as:

C7 to *C12* aliphatic, alicyclic (typically 80-85 wt.%) and aromatic hydrocarbons (typically 15-20 w/w%), with a boiling range within 90-230°C.

In connection with the REACH registrations the Hydrocarbon Solvents Producers Association HSPA has developed a new naming system for the hydrocarbon solvents. In this the three white spirits belong to the following hydrocarbon solvent group category: *C9-C14 Aliphatic (2-25% aromatic) Hydrocarbon solvent category.*

The white spirits are clear, colorless and flammable liquids with a flash point of approximately 21-68 $^{\circ}$ C. They have a density of approximately 0.8 g/ml, insignificant water solubility, and a vapor pressure in the range of 0.3-3 kPa. Further they have a distinct odor with an odor threshold of about 0.5-5 mg/m³ in air due to their high content of aromatic hydrocarbons.

Regulation and risk management measures

White spirit type 0, White spirit type 1 and Stoddard solvent are all subjected to EU harmonised classification:

Asp. Tox; H304 (May be fatal if swallowed and enters airways)..

Further *White spirit type 1* and *Stoddard solvent* should be classified with:

Carc.1B; H350 (May cause cancer) and

Mut 1B; H340 (May cause genetic effects).

These classifications as carcinogenic and mutagenic apply if it cannot be documented that the content of benzene in the solvent is less than 0.1 w/w%. However, in general the solvents are produced with lower levels of benzene and thus in practice the solvents on the market do not carry these classifications.

In addition to the harmonised classification end-points further self-classifications are used by the suppliers to the market in EU. The most widely used classifications are:

Flam. Liq 3; H 226 (Flammable liquid and vapour)
Eye Irrit. 2; H319 (Causes serious eye irritation)
STOT SE 3; H336 (My cause drowsiness or dizziness)
Aquatic Chronic 2; H411 (Toxic to aquatic life with long lasting effects)

In June 2011 the Risk Assessment Committee (RAC) at the European Chemical Agency concluded that classification with STOT RE 1 H372 (central nervous system) should be added to the harmonised classification of the three substances. This was concluded based on a Danish proposal on the three substances as Denmark since 1988, at a national level, has classified *Stoddard solvent* and *White spirit type 0* with Xn R48/20 due to chronic adverse effects on the central nervous system after prolonged and repeated exposure. According to a Danish national statutory order this national classification is still valid until the new harmonised classification with STOT RE 1 H372 (central nervous system) enters into force.

The RAC opinion has recently been implemented in the 5th ATP to the CLP regulation leading to the addition of STOT RE1 H372 to the harmonised classification of the 3 substances covered by this survey.

Due to the focus in Denmark on the chronic neurotoxic effects of white spirit (and other organic solvents) additional national regulation applies that cover these white spirits. These regulations are directed towards the content of organic solvents in paint and lacquers, as these products should be attached with a volatility code number according to their content of an organic solvent. The use of these products are then further restricted for indoor use depending on the value of the volatility code number.

Further there is a national regulation on the occupational limit value on white spirit of 145 mg/m³ and national environmental guidance value of 0.2 mg/m^3 as an imission value in air (B-værdi) and a soil and groundwater quality criteria of 25 mg/kg soil and 9 µg/L water, respectively.

Further products containing white spirit are subjected to the provisions of the EU VOC directive in relation to for certain coatings and vehicle refinishing products for cars and construction (limits in the range of 30-840 g VOC/L depending of the product) and also emissions from various industrial processes have to comply with the EU VOC emission limit values.

The allocation of eco-labelling with either the EU flower, the Nordic swan or the German Blue angel is for a variety of product types dependent of the classification of the chemical constituents and the content of VOCs. This puts strict limits to the content of white spirit in product types such *as in-door and out-door paints and varnishes; car and boat care products;* and *all-purpose cleaners.*

No initiatives on white spirit are underway in relation to the REACH processes restriction, SVHC identification, authorisation or substance evaluation.

Volumes and use

From the REACH registrations it can be seen that *white spirit type 1* is by far the substance at the highest annual tonnage level in EU in the range of 1,000,000 - 10,000,000 tonnes, while *white*

spirit type 0 is registered at an annual tonnage level of 10,000-100,000 tonnes. *Stoddard solvent* is not registered which indicates a tonnage level below 1000 tonnes per importer/ manufacturer.

White spirit is imported to Denmark as no production takes place in Denmark.

The total tonnage level for these three types of white spirit has declined in Denmark from 32,027 tonnes in year 2000 to 3,395 tonnes in year 2011 (a reduction of 89% or 28,632 tonnes).

The uses in Denmark of the white spirits containing aromatics are today (The Danish Product Registry 2011 figures) mainly (in descending order): as solvents (2358 t); in cleaning and washing agents (541 t); in paints and lacquers (341 t), as fuel and fuel additive (370 t); in surface treatment (152 t), and in non-agricultural pesticides and preservatives (77 t). However, it should be noted that these uses are spread over a total of more than 987 preparations of which about 497 are paints and lacquers.

Waste

Industrial waste and consumer waste (domestic waste) containing white spirit (or product with white spirit as ingredient) will typically be defined as hazardous waste according to the waste streams defined in the Danish Statutory order on waste, and should thus be treated as this. With the recent classification as STOT RE1; H372 all waste fractions with a content above 1% of white spirit should be considered as hazardous waste.

As waste containing white spirit does not constitute a separate fraction as such, but typically is waste containing other organic solvents or dangerous substances, the waste is not considered suitable for recycling of white spirit.

Due to the high energy content of white spirit and the waste fraction in which white spirit may occur the waste will typically be further directed to incineration and energy production.

Thus, no specific concern in relation to white spirit in the waste stream has been identified.

Environment

There are no measurable concentrations of white spirit in the environment except following spills. In the environment the hydrocarbons would due to their volatility be expected to partition largely to the atmosphere. The least volatile constituents may have a potential for partition to soil and sediment, where lowered bioavailability reduces uptake by organisms. The water solubility of the alkanes and isoalkanes (aliphatic hydrocarbons) is assumed to be too low to give rise to acute aquatic toxicity, but the aromatics are expected to have sufficient water solubility to contribute to the acute and chronic aquatic toxicity, most are however volatile and the concentrations in the aquatic environment is assumed to be low.

White spirit is readily biodegradable under aerobic conditions. Octanol/water partition coefficients ranging from 3.5 to 6.4 indicate a moderate potential for bioaccumulation. Acute toxic effects to aquatic organisms are found in the range of 1 to 100 mg/L and chronic toxicity have been found for invertebrates, fish, and algae in the range of 0.1 - 1.0 mg/L (all values based on nominal loadings). As a hydrocarbon VOC substance white spirit has a potential for photochemical troposheric ozone generation. Industrial emissions are however regulated by the VOC directive and other national regulation for industrial emissions into the air.

Thus except from spills no specific concern for white spirit in the environment has been found.

Human health effects

When exposed, white spirit may be absorbed through inhalation of vapors and though skin contact to the liquid solvent (however to a lesser extent). After absorption white spirit is widely distributed throughout the body (brain, kidney, liver and fat), preferentially partitioning into fat; the half-life in adipose tissue has been estimated to be 46-48 hours. Thus accumulation of white spirit in fat tissue including the brain occurs when exposed daily. The distribution and accumulation in the brain are considered relevant for the adverse effects on the central nervous system.

Due to the low viscosity of the solvent white spirit may after oral ingestion be aspirated into the lungs and cause serious chemical inflammation and lung damage (classification with *Asp. Tox. 1;* H304).

Following acute exposure irritation of eyes and respiratory tract may occur starting at approx. 600 mg/m³ where also signs of acute central nervous system depression leading to lack of coordination and extended response time may occur (classification with STOT SE; H336 and *Eye Irrit. 2: H319*). Further dizziness and tiredness may occur and exposure to very high concentrations of white spirit in enclosed spaces can lead to narcotic effects and in severe cases loss of consciousness. Also chest pain, cyanosis, apnea and cardiac arrest have been reported in severe cases.

The critical effects following repeated inhalation exposure to white spirit are the neurotoxic effects, which in humans after prolonged exposure may develop to chronic toxic encephalopathy. This has been documented in a series of occupational studies with painters conducted primarily in the Nordic countries in the 1970'es and 1980'es, where the exposure to white spirit was found to be associated to the reduced mental functioning and the symptoms from the central nervous system. These findings have recently been recognized at EU level in connection with the addition of STOT RE1; H372 to the harmonized classification of the substances in this survey .

It is not possible to associate the adverse effects in the central nervous system to a specific hydrocarbon fraction in white spirit. On the other hand it is also not known whether the effects may be associated to the overall mixed chemical exposure from the white spirits. So it may be assumed that the neurotoxic effects may also be associated to other types of hydrocarbon solvents although this has not been documented due to lack of data.

The content of the carcinogenic substance benzene in white spirit is controlled/regulated as classification with Carc. 1b has to apply if the content of benzene is above 0.1 w/w%. Some concern towards the carcinogenic potential of the substance itself may be expressed based on data from two experimental animal carcinogenicity studies where the animals were exposed to white spirit vapors. From the outcome of the studies it was concluded that there was some evidence for carcinogenic effects in male rats and equivocal evidence in female mice. This may be due to a cytotoxic mechanism (i.e. a lower threshold is considered to exist for the effect) and not to a genotoxic mechanism as white spirit has not shown any genotoxic potential. It remains, however, to be further assessed to which extent these not quite consistent findings may be considered strong enough for a Carc. 2 classification of white spirit.

The available experimental data on mutagenicity and reproductive toxicity do not indicate a further concern for these effects.

Human exposure

Especially exposure to white spirit by inhalation during painting operations has been studied, due to the widespread use of white spirit in paint. Overall, it is acknowledged that indoor brush and roller application of alkyd paints leads to an average white spirit concentration of around 600 mg/m³ (100 ppm), but it should be noted that without ventilation, exposure can peak at much higher levels of between 1800 and 6000 mg/m³ (300 and 1000 ppm).

Also dermal exposure may occur especially if pure white spirit is used for removal of fresh paint stains and other cleaning operations.

During polishing of metallic surfaces of stoves and during shoe polishing exposure estimates for white spirit of 150 mg/m³ to 960 mg/m³ have been made in two Danish surveys on consumer products where white spirit was found as a constituent. Exposure from dermal contact and absorption was estimated to be up to 192 mg per person per event from the stove polish. However,

this was based on assuming 100% absorption as adequate data on the skin absorption of white spirit was missing.

Human health Impact

In Denmark the occurrence of organic toxic encephalopathy has decreased dramatically in relation to many years of focus on solvent exposure in the occupational environment and specifically on the focus on white spirit: In the period 1978 to 1992 more than 5000 cases of chronic toxic encephalopathy due to long term exposure to organic solvents have been recognized as an occupational disease by the National Board of Industrial Injuries in Denmark. Today, however, this is a rarely diagnosed disease with 14 cases in the period of 2005 to 2009.

For consumers only occasionally exposed to white spirit containing products (i.e. not on an everyday basis) the risk for organic toxic encephalopathy may be considered as low, as this type of adverse effects do not develop until after many years of daily exposure.

However, especially painting of indoor surfaces may generate high exposure levels and if consumers do not use adequate respiratory protection or ventilation this may lead to acute effects such as dizziness, headache, nausea, tiredness and lack of coordination and extended response time.

Alternatives

In the paint industry there has been an overall shift from the use of white spirit based paint to water based paint for construction painting both for professional products as well as for consumer products. A similar trend has been observed in the printing industry where the use of white spirit has declined dramatically due to new technologies and use of alternatives products primarily based on plant oils and mono-esters of plant oil fatty acids.

There seems to be a further potential for substitution especially for cleaning purposes termed as: cold cleaners, automotive cleaners, and industrial degreasers where the use of mono-esters of fatty acids derived from plant oil may take over.

However, there are still areas where the substitution of white spirit containing products may be more difficult e.g. surface treatment or painting of metals and in vacuum impregnation of wood.

Substitution to other comparable hydrocarbon solvents should be undertaken with care as the toxicological properties of these solvents may be the same (although not subjected to harmonised classification). However, reduction of the risk potential for adverse effects may be gained if the substituting solvent has a lower vapor pressure and thus emits less vapors and poses a lower potential for inhalation of vapors.

Overall conclusions

The overall picture in the description of white spirit shows how common efforts from worker organizations, authorities, and NGOs in collaboration with industry and industrial development have changed the handling and use of white spirit in order to develop more safe products for workers and consumers and to establish safer working conditions for workers in occupational processes and uses where white spirit is used.

Although the use of white spirit in Denmark today has declined from round 32,000 tonnes in 2000 to round 3,400 tonnes in 2011 this is still a high volume for a dangerous substance.

Successful substitutions of white spirit with alternative substances or alternative technologies have been introduced especially within the paint industry and the printing industry. This development should continue – also for other product types - if further reduction of the use of white spirit should

be obtained. In that respect further potential for substitution may be within the various products for degreasing/ cleaning purposes.

Substitution to other comparable hydrocarbon solvents should be undertaken with care as the toxicological properties of these solvents appear to be similar to the classified ones although data may not be sufficient to warrant a harmonised classification. However, reduction of the risk potential for adverse effects may be gained if the substituting solvent has a lower vapor pressure and thus poses a lower potential for inhalation of vapours.

Concerning consumer use here may still today be situations where the use of white spirit containing products may constitute a risk for users. This may especially be in situations where surface treatment products or paints with white spirit are used in enclosed or unventilated spaces. This may due to the evaporation lead to high vapor concentrations which in severe cases may lead to risk of acute intoxications. So information to the consumer on correct use of such products has to be emphasized in order to avoid misuse.

Based on a Danish classification proposal, white spirit has recently (September 2013) been classified as STOT RE1: H372 on EU level due to its potential for chronic neurotoxic effects. This may not in itself directly affect the use in Denmark as a national legislation for this type of classification has been in place since 1988, but it may affect the overall European market and thereby have an indirect effect in Denmark as well.

Data from two carcinogenicity studies with inhalation exposure to rats and mice were interpreted by the NTP (US National Toxicology Programme) as giving some evidence for carcinogenicity in rats and equivocal evidence in mice. However, these border line and inconsistent results need further expert evaluation in order to conclude whether the data suffice for a CLP Carc. 2 classification.

No specific concern in relation to white spirit in the waste stream has been identified.

No specific concern for white spirit in the environment has been found except in cases with spill.

Sammenfatning og konklusion

Denne undersøgelse omhandler mineralsk terpentin og omfatter 3 oliebaserede kulbrintestoffer.. Begrundelsen for at medtage disse stoffer på LOUS er, at der i Danmark har været særligt fokus på disse stoffer på grund af deres farlighed mht. at medføre kroniske effekter på centralnervesystemet ("malersyndromet"). Dette kan forekomme efter lang tids erhvervsmæssig eksponering i frobindelse med indånding af terpentindampe.

Hovedformålet med denne gennemgang er at fremlægge data for den danske Miljøstyrelse, der kan danne baggrund for overvejelser om behovet for eventuelle yderligere risikohåndteringsforanstaltninger for mineralsk terpentin.

Identifikation og stoffernes fysisk-kemiske egenskaber

Mineralske terpentin er et kulbrinteopløsningsmiddel defineret som et UVCB-stof (dvs. stoffer med Ukendt eller Variabel sammensætning, Komplekse reaktionsprodukter eller Biologiske materialer). De tre stoffer udgøres således af en kompleks sammensætning af kulbrinter med et højt indhold af aromatiske kulbrinter (15-20%).

Alle tre stoffer er olieafledte stoffer, og det nøjagtige kemiske indhold afhænger af kvaliteten af råolien og de raffinaderiprocesser, stofferne har undergået. Baseret på deres stof definitionen kan de ikke skelnes fra hinanden kemisk, idet de har ens og overlappende kulbrinte-sammensætning. De tre stoffer er:

a)	Mineralsk terpentin type 0	(CAS 64742-88-7)
b)	Mineralsk terpentin type 1	(CAS 64742-82-1)
c)	Mineralsk terpentin (Stoddard solvent)	(CAS 8052-41-3)

Mineralsk terpentin type 1 er det europæiske modstykke til mineralsk terpentin, CAS 8052-41-3, (kaldet Stoddard solvent iUSA). Mineralsk terpentin type 1 er den mest udbredt anvendte mineralske terpentin med højt aromatisk indhold i Europa.

Generelt kan indholdet af de tre stoffer beskrives som: C7 til C12 alifatiske, alicycliske (typisk 80-85 vægt%) og aromatiske kulbrinter (typisk 15-20 w/w%), med et kogepunktsinterval indenfor 90-230°C.

I forbindelse med REACH registreringerne har "the Hydrocarbon Solvents Producers Association" HSPA udviklet et nyt navngivningssystem til kulbrinteopløsningsmidler. I dette system tilhører de tre typer mineralske terpentin følgende kulbrinteopløsningsmiddelgruppe kategori: *C9-C14 Alifatiske (2-25% aromatiske) Kulbrinteopløsningsmiddel kategori.*

Mineralsk terpentin er en klar, farveløs og brændbar væske med flammepunkt ved ca. 21-68 °C. Densiteten er ca. 0,8 g/ml, stoffet har meget ringe vandopløselighed og et damptryk i intervallet 0,3-3 kPa. Yderligere har mineralsk terpentin en karakteristisk lugt med lugtgrænse ved omkring 0,5-5 mg/m³ i luft på grund af det høje indhold af aromatiske kulbrinter.

Regulering og risikohandteringsforanstaltninger

Mineralsk terpentin type o, mineralsk terpentin type 1 og Stoddard solvent er alle underlagt EU's harmoniserede klassificering, med klassificeringen:

Asp. Tox; H304 (Kan være livsfarligt, hvis det indtages og kommer i luftvejene)

Desuden skal *mineralsk terpentin type 1* og Stoddard solvent klassificeres med: Carc.1B; H350 (Kan fremkalde kræft) og Mut 1B; H340 (Kan forårsage genetiske defekter)

Disse klassificeringer skal anvendes, hvis det ikke kan dokumenteres, at indholdet af benzen i opløsningsmidlet er mindre end 0,1 w/w%. Generelt produceres opløsningsmidlerne dog med lavere benzenniveauer, og dermed er opløsningsmidlerne på markedet i praksis ikke klassificeret for disse effekter.

Ud over den harmoniserede klassificering, anvender lerandørerne i EU også selv-klassificering af stofferne. De mest anvendte selvklassificeringer er: Flam. Liq 3; H 226 (Brandfarlig væske og damp) Eye Irrit. 2; H319 (Forårsager alvorlig øjenirritation) STOT SE 3; H336 (Kan forårsage sløvhed eller svimmelhed) Aquatic Chronic 2; H411 (Giftig for vandlevende organismer, med langvarige virkninger)

I juni 2011 konkluderede Udvalget for Risikovurdering ved Det Europæiske Kemikalieagentur, RAC, at klassificering med STOT RE 1 H372 (Forårsager skader på centralnervesystemet ved længerevarende eller gentagen eksponering) bør føjes til den harmoniserede klassificering af de tre stoffer. Dette blev konkluderedet på grundlag af et dansk klassificaringsforslag for de tre stoffer, idet Danmark siden 1988 på nationalt plan har klassificeret *mineralsk terpentin (CAS 8052-41-3)* og *mineralsk terpentin type 0* med Xn R48/20 på grund af kroniske skadelige effekter på centralnervesystemet efter længerevarende og gentagen eksponering. RAC udtalelsen er for nylig blevet implementeret med 5. tilpasning til CLP forordningen med tilføjelsen af STOT RE1 H372 til den harmoniserede klassificering for de 3 stoffer i denne kortlægning. Ifølge en dansk bekendtgørelse er denne nationale klassificering stadig gældende, indtil den nyligt vedtagede harmoniserede klassificering med STOT RE 1 H372 træder i kraft i Januar 2015.

Som følge af mange års dansk fokus på de kroniske neurotoksiske effekter af mineralsk terpentin (og andre organiske opløsningsmidler) er der indført en række nationale bestemmelser, der omfatter organiske opløsningsmidler og hermed mineralske terpentin. Disse bestemmelser er generelt rettet mod indholdet af organiske opløsningsmidler i maling og lak, da disse produkter skal være forsynet med et kodenummer for flygtighed i overensstemmelse med deres indhold af fordampeligt organisk opløsningsmiddel. Indendørs brug af produkterne er reguleret gennem værdien af kodenummeret for flygtighed, hvilket dermed begrænser indholdet af mineralsk terpentin.

Yderligere har Arbejdstilsynet gennem deres grænseværdi bekendtgørelse fastsat en erhvervsmæssig grænseværdi for mineralsk terpentin på 145 mg/m³ og Miljøstyrelsen har fastsat en vejledende værdi på 0,2 mg/m³ som imissionsværdi i luft (B-værdi). Derudover foreligger der fra Miljøstyrelsens side et jord- og et grundvandskvalitetskriteriefor mineralsk terpentin på henholdsvis 25 mg/kg jord og 9 µg/L vand.

Endvidere er anvendelse af mineralsk terpentin underlagt bestemmelserne i EU VOC-direktivet i forhold til indholdet i visse bygningsmalinger og -lakker samt produker til autoreperationslakering (grænser for indholdet ligger i intervallet 30 til 840 g VOC/L afhængig af produktet) og i forhold til direktiv om EU VOC emissionsgrænser for forskellige industrielle processer.

Der er p.t. ingen initiativer undervejs for mineralsk terpentin i forbindelse med REACH reguleringen, dvs i relation til SVHC identifikation, godkendelsesordningen eller prioritering til stofvurdering.

Tildelingen af miljømærkning med enten EU-blomsten, det nordiske Svanemærke eller det tyske Blå Engel er for en række forskellige produkttyper afhængig af klassificeringen af de kemiske bestanddele og VOC-indholdet. Dette sætterstrenge grænser for eller udelukker helt indhold af mineralsk terpentin i produkttyper såsom *indendørs og udendørs malinger og lakker, bil- og bådplejeprodukter samt rengøringsmidler*.

Mængder og anvendelse

Fra REACH registreringerne kan det ses, *at mineralsk terpentin type 1* er det stof, som har langt det højeste årlige tonnage-niveau i EU, i størrelsesordenen 1.000.000 - 10.000.000 tons, mens *mineralsk terpentin type 0* er registreret i et årligt tonnage-niveau på 10.000 - 100.000 tons. Stoddard solvent er ikke registreret, hvilket indikerer et tonnage-niveau under 1000 tons pr. importør/producent.

Al mineralsk terpentin bliver importeret til Danmark, da der ikke er nogen produktion i Danmark.

Ifølge oplysninger fra det danske produktretgister er det samlede tonnage-niveau for disse tre typer mineralsk terpentin i Danmark faldet fra 32.027 tons i år 2000 til 3.395 tons i år 2011 (en reduktion på 89% eller 28.632 tons).

Anvendelsen af mineralsk terpentin indeholdende aromiske kulbrinter var i Danmark i 2011 inden for følgende kategorier: som opløsningsmidler (2358 t); i rengørings- og vaskemidler (5411 t); som brændstof og brændstofadditiv (370 t); i malinger og lakker (341 t); til overfladebehandling (152 t); i ikke-landbrugsmæssige pesticider og konserveringsmidler (77 t).

Det skal bemærkes, at disse anvendelser er spredt ud på 987 produkter, hvoraf 497 er malinger og lakker.

Affald

Industriaffald og forbrugeraffald (husholdningsaffald), der indeholder mineralsk terpentin (eller produkter med terpentin som bestanddel) vil typisk være defineret som farligt affald i henhold til den danske bekendtgørelse om affald, og skal derfor behandles i overensstemmelse hermed. Med den nyligt vedtagne klassificering som STOT RE1; H372 skal alle affaldsfraktioner med indhold over 1% mineralsk terpentin såleds fremover betragtes som farligt affald.

Da affald indeholdende mineralsk terpentin ikke udgør en separat fraktion som sådan, men typisk er sammen med affald som indeholder andre organiske opløsningsmidler eller farlige stoffer, anses affaldet ikke for at være egnet til genvinding af mineralsk terpentin.

På grund af det høje energi-indhold i mineralsk terpentin og de affaldsfraktionener, hvor mineralsk terpentin kan forekomme, vil affaldet typisk blive videresendt til forbrænding og energiproduktion. Det vurderes umiddelbart at de nuværende regler og den nuværende praksis vedr. indsamling og håndtering af terpentinholdigt affald er hensigtmæssig og tilstrækkelig.

Miljø

Der anses ikke at være målbare koncentrationer af mineralsk terpentin i miljøet undtagen i forbindelse med konkrete udslip. I miljøet forventes kulbrinterne på grund af deres flygtighed hovedsageligt at afdampe til atmosfæren. De mindst flygtige bestanddele kan have et potentiale for fordeling til jord og sediment, hvor nedsat biotilgængelighed reducerer optagelsen af organismer. Vandopløseligheden af alkaner og isoalkaner (alifatiske kulbrinter) antages at være for lav til at give anledning til akut toksicitet for vandmiljøet, mens de aromatiske kulbrinter forventes at have tilstrækkelig vandopløselighed til at bidrage til akut og kronisk toksicitet for vandmiljøet, de fleste er dog forhldsvis flygtige og koncentrationerne i vandmiljøet antages at være lave. Mineralsk terpentin er let bionedbrydeligt under aerobe forhold. Log octanol/vand koefficienter er i intervallet fra 3,5 til 6,4, indikerer et moderat potentiale for bioakkumulering. Akutte toksiske effekter for vandlevende organismer er fundet i intervallet 1 til 100 mg/L, og kronisk toksicitet er fundet for hvirvelløse dyr, fisk og alger i intervallet fra 0,1 til 1,0 mg/L (alle værdier er baseret på nominelle belastninger).

Kulbrinter udgør i forbindelse med afdampning et potentiale for troposfærisk ozondannelse i forbindelse med foto-kemiske reaktioner i atmosfæren. I den forbindelse reguleres industrielle emissioner af VOC-direktivet og andre nationale regler for industrielle emissioner til luften. Mineralsk terpentin vurderes udlukkende at kunne medføre miljømæssige problemer i forbindelse med uheld og udslip til miljøet.

Sundhedsskadelige effekter

Ved human eksponering kan mineralsk terpentin optages ved indånding af dampe og ved hudkontakt med det flydende opløsningsmiddel (dog i mindre grad). Efter absorption fordeles mineralsk terpentin til kroppens organer (hjerne, nyrer, lever og fedt) med de største koncentrationer i fedtvævet. Halveringstiden i fedtvæv er anslået til at være 46-48 timer. Der opstår således ophobning af mineralsk terpentin i fedtvæv, herunder hjernen, ved daglig eksponering. Fordelingen til og akkumulering i hjernen anses for at være afgørende for de skadelige virkninger på centralnervesystemet.

På grund af opløsningsmidlets lave viskositet kan mineralsk terpentin efter indtagelse aspireres ned i lungerne og forårsage en alvorlig kemisk lungebetændelse og lungeskader (jf. klassificering med *Asp Tox 1; H304*).

Efter akut eksponering kan der opstå irritation af øjne og luftveje begyndende ved en koncetnration i luften på ca. 600 mg/m³, hvor der også kan forekomme tegn på akut påvirkning af centralnervesystemet, der kan føre til manglende koordinationsevne og forlænget reaktionstid (klassificering med *STOT SE; H336* og *Eye Irrit 2; H319*). Endvidere kan der forekomme svimmelhed og træthed, og ved eksponering for meget høje koncentrationer af mineralsk terpentin i lukkede rum kan dette medføre narkotiske virkninger og i alvorlige tilfælde bevidstløshed. Også brystsmerter, cyanose, apnø og hjertestop er rapporteret i særligt alvorlige tilfælde.

De mest kritiske effekter efter gentagen indånding af mineralsk terpentin er de neurotoksiske virkninger, som hos mennesker efter længere tids eksponering kan udvikle sig til kronisk hjerneskade. Dette er blevet dokumenteret i en række erhvervsmæssige undersøgelser med malere foretaget primært i de nordiske lande i 1970'erne og 1980'erne, hvor eksponering for mineralsk terpentin blev fundet at være forbundet med nedsatte mentale funktioner og symptomer fra centralnervesystemet. Disse resultater er for nylig blevet anerkendt på EU-plan i forbindelse med tilføjelsen med STOT RE1; H372 til den harmoniserede klassificering, som vil blive implementeret i den nærmeste fremtid.

Det er ikke muligt at konkludere om de skadelige effekter i centralnervesystemet skyldes en specifik kulbrintefraktion i mineralsk terpentin eller om effekterne er en følge af kombinationseffekterne af den samlede kemiske påvirkning. Det må derfor antages, at de neurotoksiske virkninger også kan være forbundet med andre lignende typer kulbrinteopløsningsmidler (både alifatiske eller aromiske opløsningsmidler), selv om det ikke konkret er dokumenteret på grund af manglende data.

Indholdet af det kræftfremkaldende stof benzen i mineralsk terpentin kontrolleres/reguleres, idet klassificering med Carc. 1b skal anvendes, hvis indholdet af benzen er over 0,1 w/w%. Der kan imidlertid også være en vis bekymring for stoffets evt. kræftfremkaldende effekt i forbindelse med data fra to dyre-eksperimentellecancerstudier, hvor dyrene blev eksponeret for dampe fra mineralsk terpentin. Ud fra resulteterne blev det konkluderet, at der var en vis dokumention for

kræftfremkaldende effekter i hanrotter og en usikker dokumentaion dokumentation for kræftfremkaldende effekter i hunmus, mens der ikke var nogen dokumentation for kræftfremkaldende effekter hverken i hunrotter eller hanmus. Den evt. kræftfremkaldende effekt kan mest sandsynligt skyldes en cytotoksisk mekanisme (- er en toksisk effekten der først optræder over et vist tærskel-/ eksponeringsniveau) og ikke en genotoksisk mekanisme, da mineralsk terpentin ikke har vist mutagene effekter i mutagenforsøg. Der kræves dog yderligere ekspertvurdering for at at tage stilling til, hvorvidt disse ikke helt entydige data kan betragtes som stærke nok til en Carc. 2 klassificering af mineralsk terpentin.

De tilgængelige eksperimentelle data vedrørende mutagene effekter og effekter på forplantningesevne og fosteret giver ikke grundlag for yderligere bekymring for disse effektområder.

Eksponering ved brug af produkter

Eksponering for mineralsk terpentin ved indånding af dampe under malerarbejde er blevet undersøgt som følge af den udbredte brug af mineralsk terpentin i maling. Gennem disse undersøgelser der det blevet vist , at indendørs anvendelse af pensel og rulle til påføring af alkydmaling fører til en gennemsnitlig koncentration af mineralsk terpentin på omkring 600 mg/m³ (100 ppm), men det skal bemærkes, at under maling med manglende udluftning kan der opstå spidskoncentrationer på mellem 1800 og 6000 mg/m³ (300 og 1000 ppm).

Også hudeksponering kan være udbredt , især hvis ren mineralsk terpentin bruges til fjernelse af friske malerpletter eller til andre rengøringsformål.

I to danske undersøgelser af forbrugerprodukter, hvor mineralsk terpentin var en bestanddel, blev der estimeret eksponeringsniveauer for mineralsk terpentin på 150 mg/m³ og 960 mg/m³ ved polering af metaloverflader på ovne og ved skopudsning. Eksponering ved hudkontakt blev anslået til at være op til 192 mg pr. person pr. gang ved polering af ovne. Imidlertid var denne vurdering baseret på 100% hudabsorption af mineralsk terpentin.

Sundhedsmæssige konsekvenser

I Danmark er forekomsten af kroniske hjerneskader faldet drastisk i forbindelse med de mange års fokus på opløsningsmiddeleksponering i arbejdsmiljøet, herunder mineralsk terpentin. I perioden 1978 til 1992 blev mere end 5000 tilfælde anerkendt som erhvervssygdom af Arbejdsskadestyrelsen i Danmark. I dag er det en sjældent forekommende skade, og der blev i perioden 2005 til 2009 anerkendt 14 tilfælde.

For den almindelige forbruger, der kun lejlighedsvis er udsat for produkter indeholdende mineralsk terpentin (dvs. ikke daglig), må risikoen for kroniske hejrenskader anses som yderst begrænset, da forekomst af disse effekter vil kræve mange års daglig eksponering.

Dog kan maling af indendørs overflader medførek høje eksponeringsniveauer, og hvis forbrugerne ikke anvender passende andedrætsværn eller hvis der ikke skabes udluftning, kan indanding af dampe føre til akutte effekter startende med luftvejs-og øjenirritation, svimmelhed, hovedpine, kvalme, træthed, manglende koordinationssans og forlænget reaktionstid.

Alternativer

I farve- og lakindustrien har der været et generelt skift fra anvendelse af maling baseret på mineralsk terpentin til vandbaseret maling både for professionelle produkter og for forbrugerprodukter. En lignende tendens bort fra brugen af mineralsk terpentin er set i den grafiske branche, hvor brugen af mineralsk terpentin er faldet drastisk på grund af ny teknologi og anvendelse af alternative produkter, primært baseret på planteolier og monoestere af planteolie fedtsyrer. Der synes ader fortsat at være et potentiale for substitution indenfor specielt rengøring, fx i forbindelse med rengøringsmidler inden for bilpleje, industrielle affedtningsmidler, og til andre rengøringsprocesser ved alimindelige temperaturforhold.

Imidlertid er der stadig områder, hvor substitution af produkter indeholdende mineralsk terpentin ikke er mulig eller kan være meget vanskelig at opnå, f.eks. i forbindelse med maling til metaloverflader og i forbindelse med vacuum-imprægnering af træ.

Substitution til andre sammenlignelige kulbrinteopløsningsmidler bør foretages med omtanke, da de toksikologiske egenskaber af disse opløsningsmidler kan være de samme (-også selvom de ikke er omfattet af en klassificering med STOT RE1; H372). Dog kan risikoen, for at skadelige effekter optræder, reduceres, hvis det opløsningsmiddel, der subtitureres til, har et lavere damptryk og dermed nedsætter risikoen for indånding af dampe.

Samlede resultater og konklusioner

Det overordnede billede i beskrivelsen af mineralsk terpentin viser, hvordan fælles bestræbelser fra arbejdstagerorganisationer, myndigheder og NGO'er i samarbejde med industrien og industriel udvikling har ændret håndtering og anvendelse af mineralsk terpentin. Således er der udviklet mere sikre produkter til profesionelle og forbrugere, og der er gennem omlægning af arbejdsprocesser, omtanke og ny teknologi skabet sikrere arbejdsforhold i forbindelse med processer og arbejde hvor mineralsk terpentin fortsat anvendes. Selv om anvendelsen af mineralsk terpentin i Danmark i dag er faldet fra omkring 32.000 tons i 2000 til omkring 3.400 tons i 2011, er dette fortsat et stort forbrug af et farligt stof.

Vellykkede substitutioner af mineralsk terpentin med alternative stoffer eller alternative teknologier er blevet indført særligt inden for farve- og lakindustrien og den grafiske branche. Denne udvikling bør fortsætte - også for andre produkttyper - hvis der skal opnås yderligere begrænsning af anvendelsen af mineralsk terpentin. I den forbindelse vurderes der at være yderligere potentiale for substitution inden for forskellige produkter til affedtning/rengøring.

Substitution til andre kulbrinteopløsningsmidler bør foretages med forsigtighed, da de toksikologiske egenskaber af disse opløsningsmidler kan være sammenlignelige med de stoffer der har en harmoniseret klassificering også selvom data ikke er tilstrækkelige til en klassificering med STOT RE1; H372. Dog kan risikoen, for at skadelige effekter optræder, reduceres, hvis det opløsningsmiddel, der subtitureres til, har et lavere damptryk og dermed nedsætter risikoen for indånding af dampe.

Vedrørende forbruger-anvendelse kan der i dag stadig være situationer, hvor anvendelse af produkter indeholdende mineralsk terpentin kan udgøre en risiko for brugeren. Dette kan især være i situationer, hvor overfladebehandlingsprodukter eller maling med mineralsk terpentin anvendes i lukkede eller uventilerede rum. Afdampningen kan her medføre høje koncentrationer i indndingsluften, hvilket i alvorlige tilfælde kan medføre risiko for akutte forgiftninger. Så vigtigheden af oplysning til forbrugeren om korrekt anvendelse af sådanne produkter skal understreges, for at undgå forkert brug.

Baseret på et dansk klassificeringsforslag erl mineralsk terpentin for nylig blevet klassificeret med STOT RE1;H373 på EU-niveau som følge af stoffets evne til at fremkalde kroniske hjernskader ved længere tids påvirkning. Dette vil ikke i sig selv direkte påvirke brugen i Danmark, hvor national lovgivning for denne klassificering har været anvendt siden 1988, men det kan påvirke det samlede europæiske marked og dermed også have en indirekte effekt i Danmark.

Data fra to cancerforsøg med rotter og mus har medført en hvis dokumentation for kræftfremkaldende effekter i hanrotter og hunmus, mens der ikke blev fundet nogen tilsvarende effekter i hunrotter og hanmus. Disse resultater vil imidlertid kræve nærmere ekspetvurdering for at vurdere om mineralsk terpentin bør klassificeres med Carc. 2, idet data ikke er entydige og derfor meget vanskelige at tolke.

Afslutningvis kan det noteres, at der er ikke identificeret nogen særlige problemer i forbindelse med mineralsk terpentin i affaldsstrømmen, samt at der er ikke påvist særlige problemer i i miljøet ved den nuværende anvendelse af mineralsk terpentin bortset fra hvis der opstår udslip i forbindelse med uheld .

1. Introduction to the substance

1.1.1.1 General background

Two oil derived substances, in general termed as white spirit (or mineral turpentine) are included in the LOUS from 2009. These are (*white spirit type 0*), included in 2000 and (*Stoddard solvent*), included in 2004 due to specific Danish classification of the substances. The reason for including white spirit/mineral turpentine on LOUS is concern related to chronic adverse effect on the central nervous system following repeated exposure by inhalation. This concern lead Denmark to use the safety clause of the dangerous substance directive (67/548/EC) in 1998 in order to maintain the classification of white spirit as Xn; R48/20 (Harmful: Danger of serious damage to health by prolonged exposure through inhalation).

In this report a survey has been made on white spirit. Thus, this survey covers the two white spirit substances that were included in LOUS *white spirit type 0 (CAS 64742-88-7)* and *Stoddard solvent (CAS 8052-41-3)*) plus one further substance which according to the petrochemical production method and EINECS definition contains the same spectrum of constituents as the two other white spirits. This substance, (*CAS 64742-82-1, white spirit type 1*), is the most widely used quality of white spirit with a tonnage level in Denmark far above 1000 tonnes per year.

White spirit is an oil-derived complex substance consisting of aliphatic- , alicyclic -, and aromatic hydrocarbons with carbon numbers in the range of mainly C7 to C12. The substance has for many decades been used as solvent for extraction, cleaning and degreasing as well as a component in paint, lacquers and varnishes.

In the 1970'es and 1980'es the use of white spirit in paint was heavily debated as clinical examinations and studies on painters in the Nordic countries observed an associating between exposure to white spirit and to severe adverse effects to the central nervous system, termed as chronic toxic encephalopathy (or painter's syndrome).

Furthermore, the harmonised classification of two of the white spirits includes classification as carcinogenic in category 1B if it cannot be documented that the content of benzene is controlled to a level lower than 0.1%.

1.2 Definition of the substance

As already mentioned three types of white spirit are covered in this report, as these cannot be distinguished from each other as they have similar and overlapping chemical composition. The three substances are: white spirit type 0 and Stoddard solvent - both included in the LOUS list, and a white spirit type 1. White spirit type 1, which is the most widely used white spirit in Europe, is the European term for Stoddard solvent that is an American name.

These three types of white spirit contain mainly C7 to C12 aliphatic, alicyclic (typically 80-85 wt.%) and aromatic hydrocarbons (typically 15-20 wt.%) with a boiling range within 90-230°C. The

various types of white spirit are produced as distillation fractions from naphtha and kerosene components of crude oil. The composition of the various types can vary within the specified limits as indicated in the full EC names (see below), because of differences in the raw material (crude oil) and in the production processes. These are the typical (or old) white spirit with high aromatic content.

But also other and newer types of white spirits exist, i.e. white spirit type 2 and white spirit type 3, which differ in respect to the content of aromatic hydrocarbons. These types have been subject to solvent-extraction or catalytic hydrogenation resulting in low levels (or the absence) of aromatic hydrocarbons, but are not covered in this survey as these qualities do not belong to the typical white spirit.

According to the REACH nomenclature these oil-derived substances belong to a type of substances named UVCB substances, i.e. substances of Unknown or Variable composition, Complex reaction products or Biological materials. The composition of these substances is highly dependent of the starting material and the processes used for the manufacture of the substances, and thus the composition may vary from production to production within some specified ranges. The white spirit substances as mentioned above contain hundreds of different hydrocarbon isomers in the C7 to C12 range.

In table 1-1 the substances are described on the basis of the EC/ EINECS definition.

	White spirit type o	White spirit type 1	Stoddard solvent
EC name	Solvent naphtha (petroleum), medium aliphatic. A complex combination of hydrocarbons obtained from the distillation of crude oil or natural gasoline. It consists predominantly of saturated hydrocarbons having carbon numbers predominantly in the 9- 12 range and boiling in the range of approximately 140 to 220°C.	Naphtha (petroleum), hydrodesulphurized heavy. A complex combination of hydrocarbons obtained from a catalytic hydrodesulfurization process. It consists of hydrocarbons having carbon numbers predominantly in the 7- 12 range and boiling in the range of approximately 90 to 230°C.	Stoddard solvent. A colourless, refined petroleum distillate that is free from rancid or objectionable odours and that boils in a range of approximately 148.8 to 204.4°C.
Synonyms	-	rpentine; Petroleum spirits; S acknafta (Sweden); Testbenzi nark)	*
EC number	265-191-7	265-185-4	232-489-3
CAS number	64742-88-7	64742-82-1	8052-41-3
OECD SIDS description (2012)	Includes C8 to C13 branched, linear, and cyclic paraffins and	Includes C8 to C13 branched, linear, and cyclic paraffins and	Includes C8 to C14 branched, linear, and cyclic paraffins and aromatics

TABLE 1-1

DEFINITION/ DESCRIPTION OF WHITE SPIRIT (FROM WHO/IPCS, 1996 AND ECHA, 2011)

	aromatics (14 to 20%), <50 ppm(vol) benzene	aromatics (15 to 25%), <100 ppm(vol) benzene	(6 to 18%), <50ppm(vol) benzene
Composition			

In connection with the REACH registrations of the substances a new naming system of the substances has been developed by the Hydrocarbon Solvents Producers Association (HSPA 2011), which was also applied in the OECD assessment of the substances OECD (2012).

In this naming system the hydrocarbon solvents are grouped in various categories and the three white spirit substances are placed in the overall category of:

C9-C14 Aliphatic (2-25% aromatic) Hydrocarbon solvent category

Within this category there are *five* subcategories with more narrow carbon number range in which the three types of white spirit can be placed (see details in appendix 1)

More detailed chemical descriptions of the various hydrocarbon isomers in the substances are given in Table 1 and 2 in appendix 2.

1.3 Physical and chemical properties

Below physical chemical properties of white spirit are given.

TABLE 1-2

Property	White spirit type 0	White spirit type 1	Stoddard solvent
Physical state (at 20°C and 101.3 K.Pa)	Liquid	liquid	liquid
Molecular weight	150 (average) 9	2-179 (single constituent	s)
Conversion factor		$m = 6.1 mg/m^3$ $/m^3 = 0.16 ppm$	
Boiling range (°C)	152-198 (146-299)	130- 220	159-195
Relative density (15°C)	(0.77-0.85)	0.75- 0.8	0.79
Vapour pressure (k.Pa, 20°C)	(<1-3.7 at 38°C)	0.8 -	0.285
Water solubility, w/w %)	-	negligible	negligible
Flash point (°C)	≥ 38 (29-70)	21-68	43
Explosive properties (limits in % by volume in air)	-	0.6- 7.0	0.8-5.6
Self-ignition temperature (°C)	-	>200	260
Viscosity (mm2/sec, 25 °C)	(1-2.4 at 40°C)	1-1.5	1.2

PHYSICAL CHEMICAL PROPERTIES OF WHITE SPIRIT (ECHA 2011B)

The values in parenthesis are data from the REACH registration on white spirit type o.

1.4 Summary and conclusions

Three types of white spirit with a high content of aromatic hydrocarbons are covered in this report. The substances are not chemically distinguishable from each other as they have similar and overlapping chemical composition. The three substances are:

d)	white spirit type 0	(CAS 64742-88-7)
e)	white spirit type 1	(CAS 64742-82-1)
f)	Stoddard solvent	(CAS 8052-41-3)

The full EC names for the substances are:

a) <u>Solvent naphtha (petroleum), medium aliphatic</u>. A complex combination of hydrocarbons obtained from the distillation of crude oil or natural gasoline. It consists predominantly of saturated hydrocarbons having carbon numbers predominantly in the 9-12 range and boiling in the range of approximately 140 to 220°C.

b) <u>Naphtha (petroleum), hydrodesulphurized heavy</u>. A complex combination of hydrocarbons obtained from a catalytic hydrodesulfurization process. It consists of hydrocarbons having carbon numbers predominantly in the 7-12 range and boiling in the range of approximately 90 to 230°C.

c) <u>Stoddard solvent</u>. A colourless, refined petroleum distillate that is free from rancid or objectionable odours and that boils in a range of approximately 148.8 to 204.4°C.

White spirit type 1 is the European counterpart of Stoddard solvent (US term of the substance) and is the most widely used white spirit with high aromatic content in Europe.

All three substances are oil derived substances and the exact chemical content is dependent on the quality of the raw oil and the refinery processes to which they have been subjected. However, the final content of the substances solvents is very similar and hardly distinguishable from each other. Overall the content of the three substances they can be described as:

C7 to *C12* aliphatic, alicyclic (typically 80-85 wt%) and aromatic hydrocarbons (typically 15-20 w/w%), with a boiling range within 90-230°C.

In connection with the REACH registrations the Hydrocarbon Solvents Producers Association; HSPA has developed a new naming system for the hydrocarbon solvents. In this the three white spirits belong to the following hydrocarbon solvent group category:

C9-C14 Aliphatic (2-25% aromatic) Hydrocarbon solvent category

Overall, the three white spirits are clear, colorless and flammable liquids with a flash point of approximately 21-68 $^{\circ}$ C. They have a density of approximately 0.8 g/ml, insignificant water solubility, and a vapor pressure in the range of 0.3-3 kPa. Further, they have a distinct odor with an odor threshold of about 0.5-5 mg/m³ in air due to their high content of aromatic hydrocarbons.

2. Regulatory framework

An overall description of the legal framework in relation to chemicals on a regional and international level, in EU and in Denmark is given in appendix 3. This chapter, however, focuses on regulation as well as eco-labelling in EU and Denmark relevant for white spirit as no regional or global commitments addressing white spirit have been identified.

2.1 Classification

2.1.1 Harmonised Classification

According to regulation (EC) NO 1272/2008 (the CLP regulation) the three types of white spirit have obtained EU-harmonised hazard classification as follows:

TABLE 2-1

HARMONISED CLASSIFICATION ACOORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 ACCORDING TO CLP REGULATION (AND ACCORDING TO DSD DIRECTIVE 67/548/EEC , IN BRACKETS)

Chemical identification	CAS No	Classification			
		Hazard Class and Category Code(s		Hazard Code(s)	statement
Solvent naphtha (petroleum), medium aliphatic	64742-88-7	Asp.Tox.1	(Xn)	H304	(R65)
Naphtha (petroleum), hydrosulphurized	64742-82-1	Asp.Tox.1 Muta. 1B , Note P	(Xn)	H304 H340	(R65) (R46)
heavy		Carc. 1B , Note P	t. 2, Note P) 2, Note P)	H350	(R45)
Stoddard solvent	8052-41-3	Asp.Tox.1 (Xn) Muta. 1B , Note P	9 N-4- D)	H304 H340	R(65)
		Carc. 1B , Note P	t. 2, Note P) t. 2, Note P)	H350	(R46) (R45)

H304: May be fatal if swallowed and enters airways (R65: Harmful: may cause lung damage if swallowed)

(R46: May cause heritable genetic damage)

H340: May cause genetic effects H350: May cause cancer

H350: May cause cancer(R49: May cause cancer)N o t e P: The classification as a carcinogen or mutagen need not apply if it can be shown that the substance
contains less than 0,1 % w/w benzene.

It has to be noted that the harmonised classification only has been evaluated and concluded on three preselected hazard end-points: carcinogenicity, mutagenicity and aspiration danger, and that

classification for other hazards have to be done by self-classification by the importer/manufacturer of the substance.

In June 2011 the Risk Assessment Committee at the European Chemical Agency concluded that the following classification with **STOT RE 1 H372 (Causes damage to the central nervous system through prolonged or repeated exposure)** should be added to the harmonised classification of the three substances based on a Danish proposal on the three substances. This classification has recentlyl be implemented with the fifth adaptation to technical progress to the CLP regulation which enters into force in January 2015 (EU Journal, 2013). At national level Denmark has classified *Stoddard solvent* and *White spirit type 0* with **Xn R48/20** (Harmful: danger of serious damage to health by prolonged exposure through inhalation) due to chronic adverse effects on the central nervous system after prolonged and repeated exposure since 1988 . This national classification is still valid until the new harmonised classification with STOT RE 1 H372 (central nervous system) enters into force (Danish Ministry of Environment, 2010b).

2.1.2 Notified classification

According to the CLP regulation, companies placing chemical substances or chemical mixtures on the market in EU must notify the classification they apply for the substances to the European Chemicals Agency, ECHA.

The classifications used (and notified) by the companies can be searched at the ECHA website in the CLP inventory database. The following classifications used for the three types of white spirit are given in table 2-3, 2-4 and 2-5 below. The full classification is given for each notification that is most widely used for the substances (i.e. > 100 notifiers have notified this classification).

Chemical identification	CAS No	Classification		No. of notifiers	
		Hazard Class and Category Code(s)	Hazard statement Code(s)	1732 notifiers	
Solvent naphtha (petroleum), medium aliphatic	64742-88-7	Asp.Tox.1	H304	1111 notifiers	
		Flam. Liq 3	H226	292 notifiers	
		Asp. Tox. 1	H304		
		Eye Irrit. 2	H319		
		Aquatic Chronic 2	H411		
		Acute tox. 4	H332	327 notifiers in	
		Skin Irrit. 2	H315	total using <u>also</u> one or several of	
		STOT SE	H336	these	
		Carc. 1B	H350	classifications in their notifications	
		Aquatic Chronic 1	H411		

 TABLE 2-2

 NOTIFIED CLASSIFICATIONS FOR WHITE SPIRIT TYPE 0 (FROM ECHA C&L DATABASE)

No classification at all 1 notifier

H 226: Flammable liquid and vapor

H304: May be fatal if swallowed and enters airways

H315 : Causes skin irritation

H319: Causes serious eye irritation

H332: Harmful if inhaled

H336: May cause drowsiness or dizziness

H340: May cause genetic effects

H350: May cause cancer

H411: Toxic to aquatic life with long lasting effects

TABLE 2-3

NOTIFIED CLASSIFICATIONS FOR WHITE SPIRIT TYPE 1 (FROM ECHA C&L DATABASE)

Chemical identification	CAS No	Classification		No. of notifiers	
		Hazard Class and Category Code(s)	Hazard statement Code(s)	2150 notifiers	
Naphtha (petroleum), hydrosulphurized heavy	64742-82-1	Asp.Tox.1 Muta. 1B Note P Carc. 1B Note P	H304 H340 H350	784 notifiers	
		Flam. Liq 3 Asp. Tox. 1 STOT SE 3 Aquatic Chronic 2	H226 H304 H336 H411	292 notifiers	
		Asp.Tox.1 Muta. 1B Carc. 1B	H304 H340 H350	132 notifiers	
		Flam.Liq. 1 Flam.Liq. 2 Skin Irrit. 2 Repr. 2 Acute Tox. 3 Acute Tox. 4 Aquatic Chronic 2	H224 H225 H315 H361 H331 H312 H411	939 notifiers in total using <u>also</u> one or several of these classifications in their notifications	
		No classification at all		3 notifiers	

H 224: Extremely flammable liquid and vapour

H 225:Highly flammable liquid and vapour

H 226: Flammable liquid and vapour

H304: May be fatal if swallowed and enters airways

H312: Harmful in contact with skin

H315 : Causes skin irritation

H319: Causes serious eye irritation

H331: Toxic if inhaled

H336: May cause drowsiness or dizziness

H340: May cause genetic effects

H350: May cause cancer

H361: Suspected of damaging fertility or the unborn child

H411: Toxic to aquatic life with long lasting effects

N ot e P: The classification as a carcinogen or mutagen need not apply if it can be shown that the substance contains less than 0,1 % w/w benzene.

TABLE 2-4

NOTIFIED CLASSIFICATIONS FOR STODDARD SOLVENT (FROM ECHA C&L DATABASE)

Chemical identification	CAS No	Classification		No. of notifiers	
		Hazard Class and Category Code(s)	Hazard statement Code(s)	2110 notifiers	
Stoddard Solvent	8052-41-3	Asp.Tox.1 Muta. 1B Note P Carc. 1B Note P	H304 H340 H350	1002 notifiers	
		Flam. Liq 3 Asp. Tox. 1 Eye Irrit. 2 Aquatic Chronic 2	H226 H304 H319 H411	292 notifiers	
		Asp.Tox.1 Muta. 1B Carc. 1B	H304 H340 H350	192 notifiers	
		Asp.Tox.1 Flam.Liq. 2	H304 H225	101 notifiers 523 notifiers in	
		Skin Irrit. 2 STOT SE 3	H315 H336	total using <u>also</u> one or several of these	
		Acute Tox. 3 Acute Tox. 4	H331 H302	classifications in their notifications	

H 225: Highly flammable liquid and vapour

H 226: Flammable liquid and vapour

H304: May be fatal if swallowed and enters airways

H315 : Causes skin irritation

H319: Causes serious eye irritation

H331: Toxic if inhaled

H336: May cause drowsiness or dizziness H340: May cause genetic effects H350: May cause cancer H411: Toxic to aquatic life with long lasting effects N o t e P: The classification as a carcinogen or mutagen need not apply if it can be shown that the substance contains less than 0.1 % w/w benzene.

From the notified classifications it can be seen that the most used classifications in relation to the three types of white spirit are:

Flam. Liq 3; H226 Asp. Tox. 1; H304 Eye Irrit. 2: H319 STOT SE 3; H336 Muta 1 B (note P); H340 Carc 1B (note P); H350 Aquatic Chronic 2; H411

According to the notifications in the ECHA database it can be seen that *no companys* has made notifications with STOT RE 1 (or STOT RE 2) which would be the relevant classification to apply if they had classified considering the adverse chronic effects on the central nervous system after prolonged exposure as evaluated by RAC in 2011.

From a quick search for Safety Data Sheets on Danish web sites on white spirit type 1, it can be seen from five SDSs elaborated in the period 2004 to 2012 that classification with R48 (or STOT RE 1 or 2), which is mandatory in Denmark, has been applied in two SDSs while the three other SDSs did not apply this classification.

2.2 REACH

White spirit type 0 and white spirit type 1 have been registered under REACH. Stoddard solvent has only been pre-registered.

No further REACH activities for the white spirit substances have been identified e.g. in relation to SVHC (Substance of Very High Concern) identification, authorization, restriction, or prioritization for substances evaluation.

2.3 Other existing regulation

In relation to regulatory measures, table 2-5 below gives a compilation of EU legislation as well as Danish legislation and guidances that are considered relevant in the overall risk management of white spirit.

TABLE 2-5

LEGISLATION AND REGULATORY MEASURES ADRESSING WHITE SPIRIT

Legal instrument	EU/ national	Requirements as concerns XX		
Regulation addressing products				
DIRECTIVE 2004/42/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC	EU	The "VOC" directive that aim to avoid/ reduce ozone formation potential of the VOCs in connection with photo-chemical reactions in the ambient air defines 12 subcategories for coating products applied to buildings and 5 subcategories for vehicle refinishing products for which limits are set with regard to the content of volatile organic compounds, VOC. The maximum VOC content has been set in the range of 30 - 840 g/l depending of the product.		
Danish Statutory on marketing of VOCs in paints and lacquers: <i>Miljøministeriets Bekendtgørelse nr</i> 1049 af 27/10/2005 om markedsføring og mærkning af flygtige organiske forbindelser i visse malinger og lakker samt produkter til autoreparations-lakering	DK	(implementation of dir 2004/42/EC above)		
Danish Statutory order on derivation of code numbers: Beskæftigelsesministeriets Bekendtgørelse nr 301 af 13/05/1993 om fastsættelse af kodenumre)	DK	In this statutory order the volatility code number for white spirit with max. 15% aromatics is 3. In mixtures (products) containing white spirit the volatility code may be lower depending of the content of white spirit and the other (less volatile) substances in the product. Typically the volatility code in alkyd based paints is 2 due to the content of white spirit.		
Danish Statutory order on surface treatment products: <i>Miljøministeriets Bekendtgørelse nr</i> <i>830 af 30/10/1999 om mærkning og</i> <i>begrænsning af import, salg og</i> <i>anvendelse af overfladebehandlings-</i> <i>produkter</i>	DK	Paint must not be marketed for indoor use by the general public for painting ceilings and walls if the volatility code number is above 2.		
Regulation addressing emission to environment and limit values				
COUNCIL DIRECTIVE 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic	EU	This directive of industrial emissions (and the Danish statutory order) set limits in relation to emissions of VOC from various industrial activities (e.g. rotogravure and printing; coating industries; manufacture of coatings, surface cleaning,		

solvents in certain activities and installations		pharmaceutical production etc.). Here both limits for the total weight based emissions as well as VOC concentration limits in the emitted air are set.
Danish statutory order on activities where organic solvents are used: <i>Miljøministeriets Bekendtgørelse nr.</i> 1452 af 20/12/2012 om anlæg og aktiviteter, hvor der bruges organiske opløsningsmidler	DK	
Danish guidances on industrial emissions to ambient air: Vejledning fra Miljøstyrelsen, 2/2001. Luftvejledningen. Begrænsning af luftforurening fra virksomheder	DK	An emission limit value of 300 mg/normal m ³ and a mass-flow limit of 6250 g/hr have been set for white spirit.
and Miljøstyrelsens vejledning nr. 2, 2002, B-værdivejledningen + Supplement til B-værdivejledningen 2008.	DK	An imission value for air at neighbors to the emission site (corresponding to the tolerable exposure to the general public) has been set at 0.2 mg/m^3 for white spirit.
Danish list for recommended for guidance limit for polluted soil: <i>Miljøstyrelsen (2010). Liste over</i> <i>kvalitetskriterier i relation til</i> <i>forurenet jord og kvalitetskriterier for</i> <i>drikkevand</i> *	DK	A limit value for white spirit with aromatic content i.e. white spirit type 0, white spirit type 1 and Stoddard solvent of 25 mg /kg soil has been set. In relation to white spirit polluted soil a ground water quality criteria of 9 μ g/L groundwater and a quality criteria for air above soil surface of 0.2 μ g/m ³ air have been set. The values are expressed as total level of C7-C12 hydrocarbons.
Working environment	<u> </u>	
COUNCIL DIRECTIVE 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)	EU	Set the grounds for establishing occupational limit values for chemical substances. In 2007 The Scientific Committee on Occupational Exposure Limits (SCOEL) has proposed the following value as recommended occupational limit value for white spirit: 20 ppm (116 mg/m ³) as 8 h average level 50 ppm (290 mg/m ³) as 15 min STEL level and attachment of Skin notation
Danish statutory order regarding occupational limit values: Beskæftigelsesministeriets bekendtgørelse nr 507 af 17/05/2011 om grænseværdier for stoffer og materialer med senere ændringer.	DK	Occupational limit value: White spirit CAS 8052-41-3 (mineralsk terpentin): 25 ppm (145 mg/m ³) as 8 h average

Danish statutory order regarding work with chemical agents: <i>Beskæftigelsesministeriets</i> <i>bekendtgørelse nr. 292 af 26/04/2001</i> <i>om arbejde med stoffer og materialer</i> <i>(kemiske agenser) med senere</i> <i>ændringer</i>	DK	Requirements on Safety Data Sheets, work place instructions and substitution.
Danish statutory order regarding conduct of work: <i>Beskæftigelsesministeriets</i> <i>bekendtgørelse nr 559 af 17/06/2004</i> <i>om arbejdets udførelse med senere</i> <i>ændringer</i>	DK	Describing avoidance of unnecessary exposure at the workplace and the compliance in relation to occupational limit values
Danish statutory order on work with code-numbered products : <i>Beskæftigelsesministeriets Bekendtgørelse nr. 302 af 13/05/1993 om arbejde med kodenummererede produkter</i>	DK	Professional use of alkyd based paint and varnishes (based on white spirit) are prohibited for in-door use on ceilings and walls Further specific risk management measures are required for other professional uses of product containing white spirit (or other VOCs) resulting in a volatility code number of 1 or higher
Regulation addressing waste		
Danish Statutory order on waste: Miljøministeriets Bekendtgørelsen nr. 1309 af 18/12/2012 om affald.	DK	Waste generated from manufacture or from industrial use of white spirit has according to the Danish statutory order on waste to be treated as hazardous waste if the waste contain substances in an amount that according to classification rules for chemical substances and preparations would result in classification for either physico-chemical, toxicological or environmental properties. Thus waste containing white spirit should be classified as dangerous waste down to a content of 10% (or 1%???CLP) white spirit as this is the concentration limit for the classification with R48. (STOT RE 1)

*http://www.mst.dk/Virksomhed_og_myndighed/Kemikalier/Graensevaerdier/GV_for_jord/02350600.htm

2.4 Other international regulation

White spirit solvents and its constituents are not covered as substances of concern either in connection with OSPAR nor HELCOM (see appendix 3).

2.5 Eco-labels

Eco-labelling of products with either the EU flower or the Nordic Swan may for specific products categories be dependent of classification of the substances contained in the product or the VOC content of the product. Products that have to meet these types of criteria may not be given the eco-

label if the content of white spirit exceeds either the level for classification of the product or the maximum limit for the allowed VOC content. When implementing the classification with STOT RE 1 H372 for white spirit these criteria is may further limit the attribution of the eco-labels to the products.

In table 2-6 the eco-labelling principles are indicated for the product groups in which white spirit most probably could be used. Thus the examples illustrate types of products where the content of white spirit may hinder the allocation of the eco-label.

Product category	EU flower	Nordic swan	Blue angel
Indoor paint and varnishes	Aromatic hydrocarbons < 0.1% for the ready to use product	Aromatic hydrocarbons < 0.1% for the ready to use product	VOC < 700 ppm (RAL-UZ 102, 2010)
	Max. 15-100 g VOC/l for the ready to use product Must not contain substances classified as Carc 2, Mut 2 or STOT RE 1 (or 2) < 2% content of substances classified as Aquatic Chronic 1,2, 3, 4 Commission Decision 2009/544/EC	Max. 15-100 g VOC/l for the ready to use product No substances classified as Carc 1 or 2, Mut a or 2, or STOT RE 1 (or 2) < 2% content of substances classified as Aquatic Chronic 1,2, 3, 4 (Nordic Ecolabelling 15 June 2012 version 2.2 same as Commission Decision 2009/544/EC)	
Out-door paint and varnishes	VOC < 15-100 g/L (depending of type of product) Must not contain substances classified as Mut1 or 2; Carc 1 or 2 or Rep1 or 2 (Commission Decision 13 August 2008; C(2008)4452)	+ adhesives, sealants, fillers Must not contain naphtha classified as Acute tox 1-4, or STOT RE 1 or 2 (Nordic Ecolabelling 9 October 2012, Version 1.6)	VOC < 2-10% depending of solid content of the paint Must not contain substances classified as Mut1 ,2; Carc 1,2 or Rep1,2 . (RAL-UZ 12a, 2011)
Car and boat care products	Not specifically addressed	Product should not be classified Asp toxic 1; STOT RE 1 or 2; Aquatic Chronic 1 ,2,3 or 4. Must not contain any	Not specifically addressed

TABLE 2-6

ECOLABELLING AFFECTING THE USE OF WHITE SPIRIT

Product category	EU flower	Nordic swan	Blue angel
All-purpose cleaners	Must not contain substances classified as Carc 2, Mut 2 or STOT RE 1 (or 2) or Aquatic Chronic 1,2,3,4 Commission Decision 28 June 2011; C(2011)4442)	substances classified as Mut 1 or 2, Carc 1 or 2, Rep 1 or 2 VOC content < 12 g C2H2 equivalents/kg Further calculation criteria for the maximum content of substances classified as Aquatic Chronic 1 ,2 or 3 (Nordic Eco-labelling 21 March 2012, version 5) Product should not be classified Asp toxic 1; STOT RE 1 or 2; Aquatic Chronic 1 ,2 , 3 or 4. Must not contain any substances classified as Mut 1 or 2, Carc 1 or 2, Rep 1 or 2 Further calculation criteria for the maximum content of substances classified as Aquatic Chronic 1 ,2 or 3 (Nordic Eco-labelling 2 February 2012 version 4.6)	Not specifically addressed

Detailed criteria and criteria for other product groups, where, however, the use of white spirit is less probable can be found at the web-sites:

http://ec.europa.eu/environment/ecolabel/ http://www.ecolabel.dk/ http://www.blauer-engel.de/en/index.php

2.6 Summary and conclusions

White spirit type 0, White spirit type 1 and Stoddard solvent are subjected to EU harmonised classification.

They are all three classified with: Asp. Tox; H304 (May be fatal if swallowed and enters airways).

In addition to this *White spirit type 1* and *Stoddard solvent* should be classified with: Carc.1B; H350 (May cause cancer) and Mut 1B; H340 (May cause genetic effects) This classification shall apply if it cannot be documented that the content of benzene in the solvent is less than 0.1 w/w. However, in general the solvents are produced with lower levels of benzene and thus in practice the solvents on the market do not carry these classifications.

In addition to the harmonised classification end-points further classifications have been notified to ECHA are used by the suppliers to the market in EU. The most widely used classifications are:

Flam. Liq 3; H 226 (Flammable liquid and vapour)
Eye Irrit. 2; H319 (Causes serious eye irritation)
STOT SE 3; H336 (My cause drowsiness or dizziness)
Aquatic Chronic 2; H411 (Toxic to aquatic life with long lasting effects)

It has to be noted, however, that *no company* has notified using classification with STOT RE 1 or 2 (R48/20) for white spirit.

The classification with **STOT RE 1 H372 (central nervous system**), which was adopted by the RAC in June 2011 based on a Danish proposal has recently been included in the fifth ATP to the CLP regulation and will enter into force 1 January.

A similar classification has been in place in Denmark since 1988 for Stoddard solvent and White spirit type 0 due to chronic adverse effects on the central nervous system after prolonged and repeated exposure.

This national classification classification is still valid until the new harmonised classification with STOT RE 1 H372 (central nervous system) enters into force.

Due to the focus in Denmark on the chronic neurotoxic effects of white spirit and other organic solvents additional national regulation apply that cover these white spirits. These regulations are generally directed towards the content of organic solvents in paint and lacquers, as these products should be attached with a volatility code number according to their content of a specific organic solvent. The use of these products are then further restricted for indoor use depending on the value of the volatility code number. Pure white spirit and paints and lacquers with a certain content of white spirit have a code number of 3 which imply restrictions.

Further, there is a national regulation on the occupational limit value on white spirit and national environmental guidance on imission values (B-værdi) and levels in polluted soil and groundwater.

The industrial use of white spirit is also subject to the provisions of the EU VOC directive in relation to the content in certain industrial products and in relation to the EU VOC emission limits from certain industrial processes.

No specific initiatives on white spirit are underway in relation to REACH (e.g. restrictions, SVHC identification, authorization or prioritization for substance evaluation).

With respect to eco-labelling the allocation of the EU flower, the Nordic swan or the German Blue angel label is for a variety of product types dependent of the classification of the chemical constituents and the content of VOCs.

This puts limits to the content of white spirit in product types such as: *in-door and out-door paints and varnishes; car and boat care products; and all-purpose cleaners.*

3. Manufacture and uses

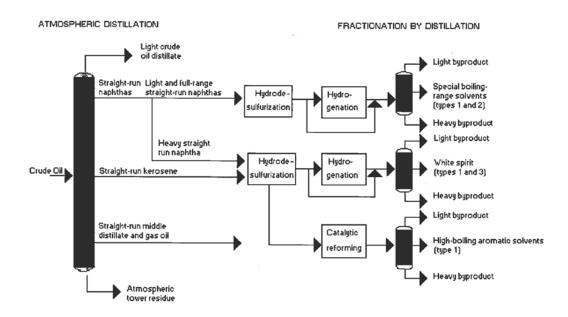
3.1 Manufacturing

3.1.1 Manufacturing processes and sites

The various types of white spirit are produced as distillation fractions from naphtha and kerosene components of crude petroleum, see figure 3-1:

FIGURE 3-1

SIMPLIFIED FLOW SCHEME FOR THE PRODUCTION OF WHITE SPIRIT AND OTHER PETROLEUM DISTILLATES (WHO/IPCS 1996).



White spirit type 0 has not been treated beyond the process of distillation of crude oil or natural gasoline (top of diagramme).

White spirit type 1 is produced from straight-run naphtha and straight-run kerosene, which are refinery process streams obtained from the distillation of crude oil. These fractions are subjected to fractional distillation into the appropriate boiling ranges of white spirit. A hydrodesulfurization process (removal of sulphur) is carried out either before or after the fractional distillation. (line 2 and 5 on the right of diagramme).

Stoddard solvent is a USA term for a hydrodesulfurised solvent which corresponds to white spirit type 1 (ECHA 2011a+b).

In Denmark no production of white spirit takes place at either of the two oil refineries, Shell in Fredericia and StatoilHydro in Kalundborg (EOF 2013, personal communication).

3.1.2 Manufacturing volumes and volumes used

Stoddard solvent is pre-registered but not registered under REACH and is listed as a low production volume chemical i.e. a tonnage level below 1000 tonnes per year in EU per manufacturer/ importer to EU.

White spirit type 0 is registered under REACH at a tonnage level of 10,000 - 100,000 tonnes per year in EU of the registrant.

White spirit type 1 is registered under REACH at a tonnage level of 1,000,000 - 10,000,000 tonnes per year in EU of the registrant. Thus white spirit type 1 is by far the most widely used type of white spirit containing aromatic hydrocarbons.

From the Nordic SPIN database the following information has been retrieved on the tonnage levels of the three qualities of white spirit:

White spirit type 0

TABLE 3-1

WHITE SPIRIT TYPE 0, TONNAGE LEVELS REGISTERED TO THE NORDIC SPIN DATA BASE, 2013

Year	Tonnage Denmark (number of mixtures)	Tonnage Nordic countries (DK+ S + N + F)
2000	3234 (1059)	27997
2002	6593 (1580)	20137
2004	491 (3059)	10087
2006	410 (1805)	7940
2008	500 (688)	5526
2010	111 (508)	2139
2011	72 (429)	1945

White spirit type 1

TABLE 3-2

WHITE SPIRIT TYPE 1, TONNAGE LEVELS REGISTERED TO THE NORDIC SPIN DATA BASE, 2013

Year	Tonnage Denmark (number of mixtures)	Tonnage Nordic countries (DK+ S + N + F)
2000	28755 (1399)	53478 (DK + S + N)
2002	31375 (2429)	65569 (DK + S + N)
2004	15979 (3973)	55284
2006	12398 (2799)	60930
2008	5288 (1778)	58876
2010	4582 (1771)	48518

2011	3245 (1544)	46303

Stoddard solvent

TABLE 3-3

STODDARD SOLVENT, TONNAGE LEVELS REGISTERED TO THE NORDIC SPIN DATA BASE, 2013

Year	Tonnage Denmark (number of mixtures)	Tonnage Nordic countries (DK+ S + N + F)
2000	38 (801)	1058
2002	3930 (1196)	4367
2004	190 (2574)	718
2006	317 (1961)	506
2008	91 (815)	606
2010	82 (794)	210
2011	78 (609)	189

Thus the total 2011 tonnage levels of the three types of white spirit in Denmark is 3,395 tonnes and in the Nordic countries approximately 48.500 tonnes. The use in Denmark is in more than 2500 products.

3.2 Import and export

3.2.1 Import and export of white spirit in Denmark

No data found. As no production of white spirit with aromatic content takes place in Denmark the substances have to be imported.

3.3 Use

White spirit is used as an extraction solvent, as a cleaning solvent, as a degreasing solvent, and as a solvent in aerosols, paints, wood preservatives, asphalt products, lacquers and varnishes (SCOEL 2007, IPCS 1996).

In table 3-4 below the uses of white spirit in Denmark are shown and divided in the most predominant use categories (data from SPIN database):

Table 3-4

most predominant uses in denmark in 2010 for white spirit with aromatic content (nordic spin data base)

	Total * tonnage/ (no of mixtures)	Solvents tonnage/ (no of mixtures)	Paint/ lacquers/ varnishes tonnage/ (no of mixtures)	Cleaning/ Washing Agents tonnage/ (no of mixtures)	Fuels tonnage/ (no of mixtures)	Surface treatment/ surface active agents tonnage/ (no of mixtures)	Non- agricultural pesticides and preservative s tonnage/ (no of mixtures)
White spirit type 0	111 (508)	-	49 (269)	-	0	20 (35)	-
White spirit type 1	4582 (1771)	3341 (43)	325 (944)	553 (75)	244 (17)	212 (121)	97 (51)
Stoddard solvent	82 (794)	-	3 (515)	-	0	3 (13)	-
Total	4775 (3073)	3341 (43)	377 (1728)	553 (75)	244 (17)	235 (169)	97 (51)

*Is indicated as total annual consumption in SPIN. As some products may belong to more than one product category they may be registered twice in different product categories and thus the addition of the volumes of the various product categories may exceed the indicated total annual consumption.

Further uses in Denmark in 2010 above 2 tonnes for *white spirit type o* are:

Impregnation materials (6t)

Further uses in Denmark in 2010 above 2 tonnes for *white spirit type 1* are:

impregnation materials (84t); corrosion inhibitors (65t); fuel additives (23); others (21t), adhesives/binding agents (16 t), fillers (4t); lubricants and additives (3t); process regulators (2t).

Further uses in Denmark in 2010 above 1 tonnes for *Stoddard solvent* are:

other uses (22 t)

Further extracts from the Danish Product Register has been made in order to obtain knowledge concerning use of the substances at various concentration levels in the product. The searches were divided in concentration bands of <1%; 1-10%; >10% for the substances and the following data as indicated in table 3-6, 3-7 and 3-8 could be retrieved.

 TABLE 3- 5

 USES OF WHITE SPIRIT TYPE O IN PRODUCTS AT VARIOUS CONCENTRATIONS (DANISH PRODUCT REGISTER, MAY

 2013)

White spirit Type O	Total	Paint/ lacquers / varnishes	Polishing / care products	Proces- sing agents	Lubricants	Impreg- nation
Content C %	tonnage/ (no of mixtures)	tonnage/ (no of mixtures)	tonnage/ (no of mixtures)	tonnage/ (no of mixtures)	tonnage/ (no of mixtures)	tonnage/ (no of mixtures)
0< C <	3.0	2.7				
1%	(78)	(40)				
1% ≤ C <	3.6	2.4				
10%	(51)	(30)				
C ≥ 10%	74 (78)	28 (46)	18(7)	5.7 (1)	5.8(-)	7.2 (3)
Total	80.6	33.1				
C > 0%	(207)	(116)				

TABLE 3-6

USES OF WHITE SPIRIT **TYPE 1** IN PRODUCTS AT VARIOUS CONCENTRATIONS (DANISH PRODUCT REGISTER, MAY 2013)

Total tonna- ge/ (no mixtu- res)	Sol- vents/ thin- ner tonna- ge/ (no mixtu- res)	Paint/ lacquer s/var- nishes tonnage / (no mixtu- res)	Fuel + addi- tives tonnage /(no mixtu- res)	Clea- ning agents tonna ge/(no mixtu- res)	Bio- cides tonna ge/(no mixtu- res)	Binders and glues tonnage /(no mixtu- res)	Surface treat- ment tonnage /(no mixtu- res)
286		6.4	277				
(169)		(91)	(15)				
246		23	35				147
(110)		(60)	(1)				(1)
3158	2335	270	20	571	77	54	
(275)	(22)	(86)	(18)	(34)	(10)	(4)	
3690		299.4					
(554)		(237)					
	tonna- ge/ (no mixtu- res) 286 (169) 246 (110) 3158 (275) 3690	kents/ hin- nertonna- ge/ (no mixtu- res)tonna- ge/ (no mixtu- res)286286(169)246(110)31582335(275)(22)3690	vents/ thin- nerlacquer s/var- nishestonna- ge/ (no mixtu- res)tonnage (no mixtu- res)2866.4(169)6.4(169)91)24623(110)10031582335(275)(22)3690Less	vents/ thin- nerlacquer s/var-snishesaddi- tivestonna- ge/ (no mixtu- res)tonnage (no mixtu- res)onnage (no mixtu- res)2866.42772866.4277(169)(10)(15)2462335(110)100(10)3158233527020(275)(22)(86)(18)3690I.299.4I.	vents/ hin- nerlacquer s/var- nishesaddi- tivesning agentstonnae ge/ (no mixtu- res)tonnage (no mixtu- 	vents/ thin- nerlacquer s/var- nishesaddi- tivesning agentsIno cidestonna- ge/ (no mixtu- res)tonnage (no mixtu- res)tonnage (no mixtu- res)tonnage ge/(no mixtu- res)tonnage ge/(no mixtu- res)tonnage ge/(no mixtu- res)tonnage ge/(no mixtu- res)tonnage ge/(no mixtu- res)tonnage ge/(no mixtu- res)tonnage ge/(no mixtu- res)tonnage ge/(no mixtu- res)tonna ge/(n	vents/ thin- nerlacquer s/var- nishesaddi- tivesning agentsIno cidesand gluestonna- ge/ (no mixtu- res)tonnage /(no mixtu- res)tonnage (no mixtu- res)tonnage ge/(no mixtu- res)tonnage (no mixtu- res)tonnage (no mixtu- res)tonnage (no mixtu- res)tonna ge/(no mixtu- res)tonna

In the C > 10% band for *white spirit type 1* further significant use volumes were used in products

for

impregnation 38.7 tonnes (5 mixtures); polish and care 22.1 tonnes (13 mixtures); corrosion inhibitors 48.5 tonnes (35 mixtures); fillers 6.5 tonnes (9 mixtures) surface treatment 4.6 tonnes (1 mixture) lubricants 5.5 tonnes (9 mixtures)

TABLE 3-7

USES OF STODDARD SOLVENT IN PRODUCTS AT VARIOUS CONCENTRATIONS (DANISH PRODUCT REGISTER, MAY 2013)

White spirit Type 1	Total	Paint/ lacquers/ varnishes	Raw Materials	Fuel additives	Solvents/ Thinners	Lubricants	Surface treatment
Concen- tration %	tonnage/ (no mixtures)	tonnage/ (no mixtures)	tonnage/ (no mixtures)	tonnage/ (no mixtures)	tonnage/ (no mixtures)	tonnage/ (no mixtures)	tonnage/ (no mixtures)
0< C <	26	1.5	23.4				
1%	(166)	(121)	(1)				
1% ≤ C <	2.2	1.1					
10%	(31)	(15)					
C ≥ 10%	52.5	5.1		38.2	1.1	2.2	5.2
	(29)	(8)		(7)	(1)	(2)	(2)
Total	80.7	7.7					
C > 0%	(226)	(144)					

Overall the following cumulated tonnage can be identified in the three concentration bands:

C < 1% :	315 tonnes (413 mixtures)
1% < C < 10%:	252 tonnes (192 mixtures)
C > 10%:	3285 tonnes (382 mixtures)

Information obtained from the Danish paint and lacquer industry indicate that the white spirit concentration can be up to 70% in oil and prime oil for surface treatment of wood. In other products where white spirit is used this is typically in the concentration range 0-40% e.g. paint for asphalt approx. 40%; primers approx. 18%; urethane paint for floors approx. 4%; and pigmented wood preservation less than 1%. White spirit is also sold in pure form or at a concentration of approx. 90% as a thinner. (DFL 2013, personel communication).

3.4 Historical trends in use

The tables 3-1, 3-2 and 3-3 clearly show an overall decrease in the use of the three types of white spirit in the Nordic countries and in Denmark during the period of 2000 to 2010. In Denmark the decrease was from a total tonnage level of 32027 tonnes in 2000 to a level of 4775 tonnes in 2010. However, the number of preparations in which the solvents were used declined in the same period only from 3259 to 3073.

An overview of the trend in Denmark is given in table 3-8 below. In this table, *white spirit type 3* (a white spirit *without* aromatic hydrocarbons) is also included as this is a newer quality of white spirit *without aromatic content* (also known as non-odorous white spirit. (The use of white spirit type 3 will be further discussed in section regarding alternatives). As seen from the table, the general trends indicate that in connection with the decline of the use of the conventional white spirits the use of white spirit type 3 has increased.

TABEL 3-8

TREND IN THE USE OF WHITE SPIRIT IN DENMARK IN THE PERIOD FROM 2000 TO 2010 (FROM THE NORDIC SPIN DATA BASE)

	White spirit type O	White spirit type 1	Stoddard solvent	Total White spirit with aromatics	White spirit type 3 (aromatic free) CAS 64742-48-9
Tonnage level 2000	3234	28755	38	32027	8500
(Number of mixt.)	(1059)	(1399)	(801)	(3259)	(1095)
Tonnage level 2010	111	4582	82	4775	65379*
(Number of mixt.)	(508)	(1771)	(794)	(3073)	(2246)
Tonnage level 2011	72	3245	78	3395	12382
(Number of mixt.)	(429)	(1544)	(609)	(2582)	(1913)
Trend 2000-2011	-3162	-25510	+40	-28632	+3882
(number of mixt.)	(-630)	(+145)	(-192)	(-677)	(+818)

*The Danish use of white spirit type 3 in <u>2010</u> is mainly in products for corrosion inhibition as 50284 tonnes were used for that purpose leaving 15095 tonnes for other product categories; see also section 7 with information on alternatives.

Older data on the consumption of white spirit with aromatic content show an annual consumption in the late 1960-ties of around 34,000 tonnes. This declined to an annual consumption of around 29,000 tonnes in the 1970'es and then went further down to around 26,000 tonnes in the early 1980'es (Danish EPA, 1986). Interestingly, these consumption volumes are rather comparable to the consumption volume in year 2000, thus the steepest decline in consumption of white spirit with aromatic content can be observed in the period from year 2000 to year 2010.

3.5 Summary and conclusions

White spirit type 0, white spirit type 1 and Stoddard solvent are generally termed as white spirits with a high aromatic content (up to approx. 20%).

From the REACH registrations it can be seen that *white spirit type 1* is by far the substance at the highest annual tonnage level in EU in the range of 1,000,000 - 10,000,000 tonnes, while *white spirit type 0* is registered at an annual tonnage level of 10,000-100,000 tonnes for the registrant.

Stoddard solvent is not registered which indicates a tonnage level below 1000 tonnes per potential registrant.

This pattern is also reflected by the common Nordic Product Registry, SPIN, where the 2011 tonnage levels in the Nordic countries for white spirit type 1, white spirit type 0 and Stoddard solvent where at 46303 tonnes, 1945 tonnes, and 189 tonnes, respectively.

The total tonnage level for these three types of white spirit has declined in Denmark from 32,027 tonnes in year 2000 to 3,395 tonnes in year 2011 (a reduction of 89% or 28,632 tonnes). However, at the same time the level of white spirit type 3 (aromatic free white spirit, which has been used to substitute white spirit with aromatics) increased from 8,500 to 12,382 tonnes (an increase of 45% or 3,882 tonnes). (In years with very high consumption of white spirit type 3 this extra volume was used for corrosion inhibition.)

The use in Denmark of white spirits containing aromatic is according to the Danish Product Registry 2013, see table 3.3 - 3.7, mainly (in descending order): as solvents (2358 tonnes); in cleaning agents (541 tonnes); in paints and lacquers (341 tonnes) as fuels and fuel additives (370 tonnes); in surface treatment (152 tonnes) and in non-agricultural pesticides and preservatives (77 tonnes). However, it should be noted that these uses are spread over a total of 987 products of which 497 are paints and lacquers.

4. Waste management

4.1 Waste from manufacture and use of white spirit

Waste generated from manufacture or from industrial use of white spirit has according to the Danish statutory order on waste to be treated as hazardous waste if the waste contains substances in an amount that according to classification rules for chemical substances and preparations would result in classification for either physico-chemical, toxicological or environmental properties (Danish Ministry of Environment 2012).

Thus, waste containing white spirit in an amount that would result in classification as hazardous should be treated as hazardous waste and be disposed/treated according to the instructions from local communities. In the future when classification with STOT RE 1 applies this will have the implication that all waste containing more than 1% of white spirit should be considered as hazardous waste.

The following waste categories (EAK- codes) described in the Danish statutory order may be especially relevant for white spirit containing waste:

Waste EAK codes	Waste fraction
03 02 05	Waste from wood preservation products containing hazardous substances
04 01 03	Waste from leather and textile industry. Waste from defatting containing organic solvents without liquid phase
07 01 04; 07 02 04; 07 03 04; 07 04 04; 07 05 04; 07 06 04; 07 07 04	Waste from various chemical processing using organic chemical solvents (codes: all termed as other organic solvent from various different process)
08 01 13; 08 01 17; 08 01 19; 08 01 21; 08 04 13; 08 04 15	Waste from manufacture of, formulation of, distribution of, use or removal of paints, lacquers and ceramic enamels and adhesives, fillers and printing inks
11 01 13	Waste from surface treatment of metals and other surfaces (waste from defatting and containing dangerous substances
12 01 09	Halogen-free cutting oil emulsions and solutions
13 07 03	Waste from liquid fuels (other fuels)

13 08 99	Other oil derived waste, not specified elsewhere
14 06 05	Waste of organic solvents, refrigerants and propellants. Other solvents and mixed solvents
16 07 08; 16 07 09	Waste from cleaning of transport tanks and vessels. Oil containing waste.Waste with other dangerous substances
20 10 13; 20 01 27	Municipal waste (domestic waste, commercial waste, waste from industries and institutions covering separate waste fractions. Solvents. Paints, inks, adhesives and, resins containing dangerous substances.

It is assumed that waste containing white spirit from consumer uses will enter into the waste stream through the municipal collection of domestic waste i.e. through the codes *20 10 13* and *20 10 27*.

4.2 Waste products from the use of white spirit in mixtures and articles

Due to the widespread use of white spirit in products a significant amount of waste containing white spirit (e.g. paint and solvent residues) may derive from consumer use. Thus a significant amount may go into the municipal collection and treatment of domestic waste under a separate waste flow for paint/ lacquer residues and organic solvents. The level of white spirit in the various types of products can be seen in section 3 divided in concentration bands of < 1%; 1-10% and > 10% content of white spirit.

The waste fractions containing white spirit may contain many other types of organic solvents and also a lot of suspended material and therefore the waste fractions are not considered suitable for recycling (Esbjerg Kommune 2012). As these waste fractions constitute an energy source they typically are subjected to incineration and energy production.

At Nord (a waste incineration plant) only sparse information specifically addressing the volume of white spirit is available as the waste with white spirit is a fraction of the waste with organic solvent. Industrial waste volumes with white spirit from single costumers is in each case less than 50 tonnes per year. The solvents are incinerated at 1100 degree Celsius. (Nord 2013, personal communication).

4.3 Release of white spirit from waste disposal

Waste containing white spirit is not suitable for land disposal, as the constituents may evaporate into air or leak into the soil. The hazardous waste containing white spirit will as chemical waste, and also due to its high energy content typically go to waste incineration and energy production and therefore not be disposed.

4.4 Summary and conclusions

Industrial waste and consumer waste (domestic waste) containing white spirit (or product with white spirit as ingredient) will typically be defined as hazardous waste according to the waste streams defined in the Danish Statutory order on waste, and should thus be treated as this. As waste containing white spirit does not constitute a separate fraction as such but typically is mixed with other waste containing other organic solvents the waste is not considered suitable for recycling of white spirit.

Due to the high energy content of white spirit and the waste fraction in which white spirit may occur the waste will typically be further directed to incineration and energy production.

5. Environmental effects and exposure

The information sources to this overview on environmental effects and exposure of white spirit are the WHO/IPCS evaluation on white spirit from 1996 and the recent OECD assessment of C9-C14 aliphatic (2-25% aromatic) hydrocarbon solvent category from 2012 which includes the three white spirits (WHO/IPCS 1996; OECD 2012). Thus the approach for the description of environmental effects of white spirit is not a systematic and detailed split up in the various chemical fractions and a detailed description of each of these hydrocarbon fractions which also would be a relevant approach, whereas the approach used by WHO/IPCS (1996) and OECD (2012) is a more overall approach looking at effects from exposure of white spirit as such i.e. as a complex mixture of hydrocarbon constituents.

White spirit is an oil-derived complex substance consisting of aliphatic, alicyclic, and aromatic hydrocarbons with carbon numbers in the range of mainly C7 to C12. The water solubility of the alkanes and isoalkanes (aliphatic hydrocarbons) is assumed to be too low to give rise to acute aquatic toxicity, but the aromatics are expected to have sufficient water solubility to contribute to the acute aquatic toxicity, most are however volatile and the concentrations in the aquatic environment is assumed to be low.

In addition to the available data for substances in this category, as defined in section 1, data for the following analogues are also presented, as necessary, to support the characterization of selected endpoints:

CAS RN 90622-57-4; Hydrocarbons, C10-C12, isoalkanes, <2% aromatics CAS RN 90622-58-5; Hydrocarbons, C11-C13, isoalkanes, <2% aromatics CAS RN 8008-20-6 ; JP-8 (having a carbon range of 8-16 and ~25% aromatics) CAS RN 64742-81-0 ; Kerosine, petroleum, hydrodesulfurized (C9-C16, wide cut UVCB)

5.1 Environmental hazard

There have been very few studies on the toxicity of white spirit to organisms in the environment. LC50 values in the order of 0.5 to 5 mg/L have been reported for aquatic organisms either for white spirit or for related hydrocarbon mixtures. There are difficulties in obtaining meaningful results from such tests with volatile materials.

Although limited data are available, it may be shown that category members are expected to exhibit acute toxic effects to aquatic organisms in the range of 1 to 100 mg/L, based on nominal loading levels, with three studies with category members and three studies with an analogue substance. A chronic study with Daphnia magna and a substance in the C9-C13 range (C9-13 mixed aliphatics and aromatics (19% aromatic)) indicated a 21-day NOEL of 0.28 mg/L, based on nominal loading levels. Additional chronic work using fish with the analogue JP-8 (C8-C16 range) indicate an NOEC = 1 mg/L based on measured concentration for a warm water fish, and a NOEC <1.4 mg/l (LOEC = 1.4 mg/L) for a cold water fish. Chronic studies using Daphnia magna with analogue substances in the C10-C12 isoparaffinic range (CAS RN 90622-57-4) indicated an effect (NOEC = 0.025mg/L,

based on measured concentration), but isoparaffins in the C11-C13 range showed no observed effects up to 1 mg/L (highest nominal loading tested) for CAS RN: 90622-58-5. QSAR values for the representative constituents were generated using EPISuite version 4.10. Acute 96-hour fish toxicity ranged from <0.01 to 3.4 mg/L. Acute 48-hour daphnid toxicity ranged from <0.01 to 2.4 mg/L. And acute 96-hour algae toxicity ranged from <0.01 to 2.3 mg/L. The model indicated that water solubility of the alkanes and isoalkanes may be too low to give rise to acute aquatic toxicity, but the aromatics are expected to have sufficient water solubility to contribute to the acute aquatic toxicity. Calculated values for the aromatic constituents, which are believed to drive the acute aquatic toxicity, ranged from 1.4 to 3.4 mg/L for fish, 1.1 to 2.4 mg/L for daphnids, and 1.3 to 2.3 mg/L for algae (OECD 2012).

Specific data on acute and chronic aquatic toxicity are given in tables 5-1 and 5-2.

TABLE 5-1

SELECTED DATA THAT CHARACTERIZE THE ACUTE AQUATIC TOXICITY OF MEMBERS OF THE C9-C14 ALIPHATIC HYDROCARBON SOLVENTS [2-25% AROMATIC] CATEGORY (OECD 2012)

Substance (CAS No.)	Freshwater Fish 96-hr (mg/l)	Freshwater Invertebrate (Daphnia magna) 48-hr (mg/l)	Freshwater Alga (Pseudokirchneriella subcapitata) 72-hr (mg/l)
Stoddard solvent (CAS RN 8052-41-3). Hydrocarbons, C9-C13 (aromatics 19%)		96-hr LL50 = 3.5 (Chaetogammarus marinus)	EbL50 = 2.5 EbC50 = 0.58 ErL50 = 5.5 ErC50 = 1.2 NOELR(b,r) = 0.76 NOEC(b,r) = 0.16
Hydrocarbons, C8-C12, n-alkanes, isoalkanes, cyclics, aromatics (2- 25%) CAS RN 64742-82-1	LL50 = 41.4 LC50 = 2.5	3 - 10 (EL50)	EL50=1 - 3 (growth rate) EL50=1 - 3 (biomass) NOEL = 1.0 (growth rate and biomass)
Kerosine, Hydrodesulphurized, C8- C15, aromatics (2-25%) CAS RN 64742-81-0 (read-across)	LL50 = 25	EL50 = 1.4	IrL50 = 8.3 IbL50 = 15 NOEL(b,r) = 4.0 (growth rate and biomass)

TABLE 5-2

Test Materials (CAS No.)	Freshwater Fish (mg/L)	Freshwater Invertebrate <i>(Daphnia magna)</i> 21-day (mg/L)	Freshwater alga (Pseudokirchneri ella subcapitata) 96-hr (mg/L)
Stoddard solvent (8052-41-3) Hydrocarbons, C9-C13 (aromatics 19%)		EiL50 = 1.62 EiC50 = 0.43 ErepL50 = 1.19 ErepC50 = 0.33 NOELRig = 1.4 NOECig = 0.37 NOELRrep = 0.28 NOECrep = 0.10	NOELR(b,r) = 0.76 NOEC(b,r) = 0.16
JP-8, C8-C16, aromatics (25%) CAS RN 8008-20-6	NOEC = 1.0 (J. floridae) NOEC < 1.4 LOEC = 1.4 (O. mykiss)		
Hydrocarbons, C10-C12, isoalkanes, <2% aromatics CAS RN 90622-57-4		NOECrep = 0.025	
Hydrocarbons, C11-C13, isoalkanes, <2% aromatics CAS RN 90622-58-5		NOELrep = 1	

SELECTED DATA THAT CHARACTERIZE THE CHRONIC AQUATIC TOXICITY OF MEMBERS OF THE C9-C14 ALIPHATIC HYDROCARBON SOLVENTS [2-25% AROMATIC] CATEGORY (OECD 2012)

LLx Lethal Loading rate (Effect concentration in test based upon water accommodated fraction (WAF))

EL_x Effect Loading rate

Ι Immobilization Reproduction

Rep Immobilization and growth Ig

b biomass

r growth rate

The solvents possess properties indicating a potential hazard for the environment (acute toxicity for fish, invertebrates, and algae (in the range of 1 to 100 mg/L) based on nominal loadings; available chronic toxicity data for invertebrates, fish, and algae are in the range of 0.1 - 1.0 mg/L, based on nominal loadings, not excluding that some members of the category might have a toxicity below 0.1 mg/L.

5.1.1 Classification

As described in section 2.1.2 no harmonised classification is available with regards to environmental hazard.

According to the CLP regulation Companies putting chemical substances or chemical mixtures on the market in EU must notify the classification they apply for the substances to the European Chemicals Agency, ECHA. When classified for environmental effects the most used environmental classification was Aquatic Chronic 2, H411, see table 5-3.

TABLE 5-3 NOTIFIED CLASSIFICATIONS FROM ECHA C&L DATABSE WITH REGARDS TO ENVIRONMENTAL

 CLASSIFICATION

Chemical identification	CAS No	Classifica	Classification	
		Hazard Class and Category Code(s)	Hazard statement Code(s)	
White spirit type O	64742-88-7	Aquatic Chronic 2	H411	452 of a total of 1732 notifiers
White spirit type 1	64742-82-1	Aquatic Chronic 2	H411	864 of 2150 notifiers
Stoddard Solvent	8052-41-3	Aquatic Chronic 2	H411	552 of 2110 notifiers

H411: Toxic to aquatic life with long lasting effects

5.2 Environmental fate

There are no measurable concentrations of the constituents in white spirit in the environment except following spills. However, the constituent compounds would be expected to partition largely to the atmosphere. Less volatile constituents partition to soil and sediment, where lowered bioavailability reduces uptake by organisms. White spirit is readily biodegradable under aerobic conditions. Octanol/water partition coefficients ranging from 3.5 to 6.4 indicate moderate potential for bioaccumulation. No studies have measured bioconcentration factors; however, because of the reported fate studies, these would be expected to be low in the field (WHO/IPCS 1996).

Members of the C9-C14 Aliphatic [2-25% aromatics] Hydrocarbon Solvents Category have the potential to volatilize from surface waters, based on Henry's Law constants representing volatility for category members that range from 46 to $9.7 \cdot 10^5 \text{ Pa} \cdot \text{m}^3/\text{mole}$ (at 25°C) [It should be noted that this broad range covers both volatile and non-volatile properties]. In the air, category members have the potential to rapidly degrade through indirect photolytic processes mediated primarily by hydroxyl radicals (*OH) with calculated degradation half-lives ranging from 0.42 to 1.10 days or 10.8 to 26.4 hours based on a 12-hr day and an *OH concentration of 1.5 x 10⁶ *OH/cm³. Aqueous photolysis and hydrolysis will not contribute to the transformation of category chemical constituents in aquatic environments because they are either poorly or not susceptible to these reactions. These chemicals are unlikely to degrade by hydrolysis as they lack a functional group that is hydrolytically reactive (OECD 2012).

When released primarily to the air compartment, the primary mode of removal would be via indirect photodegradation. Although the substances and their chemical constituents demonstrate a range of water solubility with most constituents having relatively low solubility, wet deposition of category chemical constituents is not likely to play a significant role in their atmospheric fate because of their rapid photodegradation. Volatilization to the air can contribute to the loss of category chemical constituents from aqueous and terrestrial habitats (OECD 2012).

Determining the biodegradation potential of UVCBs can be challenging. The result for each multiconstituent substance (UVCB) characterizes the biodegradability of that substance as a whole, but it does not suggest that each constituent of the UVCB is equally biodegradable. As with all ready biodegradation test guidelines, the test system and study design used with these substances (OECD TG 301F) are not capable of distinguishing the relative contribution of the substances' constituents to the total biodegradation measured (constituents with higher branching/cyclic structures may degrade to a lesser extent than linear and less branched structures). The n-paraffin constituents have the potential to biodegrade rapidly based on results that support their characterization as readily biodegradable (80 to 83% in 28 days). In comparison, iso-paraffinic constituents are expected to demonstrate a slower rate of biodegradation based on results for an analogue isoparaffinic substance, which was shown not to be readily biodegradable, but did demonstrate a moderate extent of biodegradation (41%) over an extended period of time (41 days). A multiconstituent member of the category, a C9-13 mixed aliphatics and aromatics (19% aromatic) substance (CAS RN. 64742-82-1), biodegraded to an extent of 75% after 28 days and was readily biodegradable based on a study that used the OECD 301F test guideline. The overall conclusion for C9-C14 Aliphatic [2-25% aromatics] Hydrocarbon Solvents Category members: some components of the category members (e.g. n-paraffins) are readily biodegradable, but some (tertiary and quaternary branched components) components may be less biodegradable, not meeting the readily biodegradable criteria (OECD 2012).

Mackay Level III modelling indicates that category member constituents partition mostly to the soil and water compartments rather than air compartment when an equal emission rate (1000 kg/hr) to the air, water, and soil compartment is assumed. When release occurs only to either the air, water, or soil compartment, constituents are indicated in the modelling to partition largely to the compartment to which they are released (OECD 2012).

Category members have a potential to bioaccumulate, based on calculated log BCF values for constituents that range from 2.15 to 4.06, and calculated BCF values of 142 to 11,430 L/kg wet-weight that take into account biotransformation of the chemicals in fish tissue. Results of BCF studies for several constituent chemicals of category members are also available. Reported BCF ranges for n-dodecane of 240 to 2870 L/kg wet weight, using carp and rainbow trout. Also reported is a BCF value for iso-nonanes of 1468 L/kg wet weight with carp. Additional studies for other constituent chemicals were reported for trimethylbenzene and 1,2,3,4-tetrahydronaphthalene, with values of 154 to 783 (carp and trout), and 147 to 536 L/kg (carp), respectively. Determining the bioaccumulation potential of UVCBs can be challenging. BCF values for n-paraffins, iso-paraffins, and cycloparaffins can be different due to differences in metabolism. Constituents with higher branching/cyclic structures may therefore bioaccumulate to a greater extent than linear and less branched structures. It should be noted that for highly lipophilic constituents uptake through the diet may exceed the direct uptake through water (OECD 2012).

Some members have a potential to bioaccumulate. Some components of the category members (e.g. n-paraffins) are readily biodegradable, but some components (tertiary and quaternary branched components) may be less biodegradable, not meeting the readily biodegradable criteria.

The lower molecular weight alkanes and aromatics tend to volatilize and undergo photodegradation in the atmosphere. The higher molecular weight alkanes and cycloalkanes tend to be sorbed to organic matter in soil or water. The lower molecular weight alkanes may also be sorbed in to organic matter if volatilization is not rapid (WHO/IPCS 1996).

5.3 Environmental exposure

5.3.1 Sources of release

White spirit (Stoddard solvent) may be released to the environment during its use as a solvent in dry-cleaning plants or as an industrial degreasing agent. It may also enter water or soil as a result of storage leaks or spills during use or transportation (WHO/IPCS 1996).

5.3.2 Monitoring data

There are few data on white spirit in air, water or soil. Monitoring at a site contaminated with spilt white spirit (Stoddard solvent) revealed soil levels of up to 3600 mg/kg and deep soil water levels of up to 500 mg/L. Biodegradation led to a 90% reduction in soil concentration over a 4-month period following remediation (WHO/IPCS 1996).

5.4 Summary and conclusions

There are no measurable concentrations of white spirit in the environment except following spills. The constituents in white spirit are expected to partition largely to the atmosphere. Less volatile constituents partition to soil and sediment, where low bioavailability reduces uptake by organisms. White spirit is readily biodegradable under aerobic conditions.

Results of BCF studies for several constituent chemicals are available, and the reported BCF ranges for n-dodecane of 240 to 2870 L/kg wet weight, using carp and rainbow trout. Also reported is a BCF value for iso-nonanes of 1468 L/kg wet weight with carp. These BCF values indicate moderate to high potential for bioaccumulation.

Even though limited data are available, acute toxic effects to aquatic organisms in the range of 1 to 100 mg/L were reported, based on nominal loading levels. Available chronic toxicity data for invertebrates, fish, and algae are in the range of 0.1 - 1.0 mg/L, based on nominal loadings. This would lead to a classification with Aquatic Chronic 2; H411 based on ready biodegradability and lowest chronic NOEC of ≤ 1 mg/L.

Overall, the water solubility of the alkanes and isoalkanes (aliphatic hydrocarbons) is assumed to be too low to give rise to acute aquatic toxicity, but the aromatics are expected to have sufficient water solubility to contribute to the acute and chronic aquatic toxicity, most are however volatile and the concentrations in the aquatic environment is assumed to be low. In case of spills however toxic effects and bioaccumulation in the environment can be expected.

6. Human health effects and exposure

6.1 Human health hazard

6.1.1 Classification

As described in section 2.1 white spirit on the European market is currently in general classified and labeled for the following human health hazards:

Asp. Tox. 1; H304 (May be fatal if swallowed and enters airways)

Eye Irrit. 2: H319 (Causes serious eye irritation)

STOT SE 3; H336 (My cause drowsiness or dizziness)

In near future, however, a further classification should be assigned to the substances:

STOT RE 1; H372 (Causes damage to the central nervous system through prolonged or repeated exposure)

Below the toxicological properties of white spirit are shortly described. The description is based on the information and the conclusion made by three expert groups:

WHO/IPCS (1996). White Spirit (Stoddard Solvent). Environmental Health Criteria 187. International Programme on Chemical Safety, World Health Organization, Geneva.

SCOEL (2007). Recommendation of the Scientific Committee on Occupational Exposure Limits for "White Spirit". SCOEL/SUM/87, August 2007.

ECHA (2011a+b). Committee for Risk Assessment: RAC Opinion proposing harmonised classification and labelling at Community level of white spirit.

6.1.2 Absorption, distribution and elimination

White spirit is readily absorbed into the blood stream following inhalation of the vapor. After skin contact white spirit is absorbed to a lower, but still significant extent. (Due to data on the skin absorption the classification as STOT RE1; H372 was by the Risk Assessment Committee at ECHA considered relevant for all exposure routes and therefore not specifically addressed to inhalation exposure alone).

The aromatic hydrocarbons are generally more soluble in blood than aliphatic and alicyclic hydrocarbons. White spirit is widely distributed throughout the body of humans (brain, kidney, liver and fat), preferentially partitioning into fat; the half-life in adipose tissue has been estimated to be 46-48 hours. Although the aliphatic and alicyclic hydrocarbons are absorbed to a lesser extent than the aromatic hydrocarbons, higher levels of the aliphatic and alicyclic hydrocarbons are detected in the brain compared to the levels of aromatic hydrocarbons. This may be due to differences in biological affinity and solubility or different metabolic rate in the tissues. The main metabolic pathway for both aliphatic and aromatic compounds is by oxidation to alcohol, ketone/aldehyde or carboxylic acid, which may then be conjugated prior to excretion. The excretion is mainly via the urine, with

a minor proportion via exhaled air (ECHA 2010b).

Absorbed white spirit from acute exposure will be eliminated from the body within a few days. Regular and daily occupational exposure will lead to accumulation of white spirit in fat tissue, including the brain (WHO/IPCS 1996).

6.1.3 Acute effects

Due to the low viscosity of the solvent white spirit may after oral ingestion be aspirated into the lungs and cause serious chemical inflammation and lung damage.

In humans white spirit has low acute toxicity by the inhalation, dermal and oral routes. Central nervous system depression following acute exposure may lead to lack of coordination and extended response time. Dizziness and tiredness were reported following a 7-h experimental exposure to 600 mg/m³ (100 ppm). Exposure to very high concentrations of white spirit in enclosed spaces can in severe cases lead to narcotic effects and loss of consciousness. Further, chest pain, cyanosis, apnea and cardiac arrest have been reported in these severe cases.

White spirit is a slight to moderate irritant to skin in humans. Prolonged or repeated exposure to the liquid solvent can lead to severe irritant dermatitis due to defatting. This potential may justify using the risk phrase EUH066 (Repeated exposure may cause skin dryness or cracking). Slight irritation of the eye, nose and throat has been reported in experimental studies with humans starting at a vapor concentration at 600 mg/m³ (100 ppm).

In occupational studies increased reporting of acute symptoms such as nausea, mucous membrane irritation, vertigo, and impaired sense of smell have been observed at an estimated average exposure level of 232 mg/m^3 (20 ppm).

These acute effects are reflected in the notified classification of white spirit where classification as:

Asp Tox. 1, H304 (May be fatal if swallowed and enters airways) Eye Irrit. 2, H319 (Causes serious eye irritation) STOT SE 3, H336 (May cause drowsiness or dizziness) are typically used.

6.1.4 Chronic effects, long-term exposure

The critical effects following repeated inhalation exposure to white spirit are the neurotoxic effects, which in humans after prolonged exposure may develop to chronic toxic ncephalopathy .

Numerous studies have been performed involving painters with long-term exposure to white spirit. Increased incidence of complaints of memory impairment, fatigue, impaired concentration, irritability, dizziness, headache, anxiety and apathy have been demonstrated in several cross-sectional studies. Studies including neuropsychological clinical tests have shown impaired ability in performance of some of the tests. In some studies, an overall reduction in cognitive functioning was noted to a degree that corresponded to a diagnosis of chronic toxic encephalopathy.

Similar complaints and neuropsychological test results, although more severe, were reported from clinical studies in which painters predominantly exposed to white spirit had been referred as patients to occupational medical clinics for detailed examinations.

The adverse neurotoxic effects of white spirit, including disabling and irreversible effects on mental functioning, have been demonstrated by many different investigators and in different countries. It is unlikely, therefore, that the combined set of findings could be explained by other factors.

As strong support to a causal relationship between effects on the central nervous system and longterm exposure to white spirit is that dose-response relationships for different end-points have been demonstrated in some of the epidemiological studies. In these studies exposure was graded into different subgroups or individual exposure indices were estimated, see appendix 5 with a compilation of the studies made by ECHA 2011a.

Overall, these data in 2011 led the Risk Assessment Committee at ECHA to conclude that white spirit should be classified as STOT RE 1; H372 (Causes damage to the central nervous system through prolonged or repeated exposure) but only for the qualities with aromatics. Although the classification proposal from the Danish EPA also proposed a similar classification for white spirit without aromatics this was not supported by RAC, as no specific data were available for these qualities

The Danish classification proposal covered all types of white spirit as neither WHO/IPCS (1996) or SCOEL (2007) did make separate conclusions on the varies types of white spirit, thus, the conclusion regarding the neurotoxic potential of white spirit covered white spirit with aromatics as well as white spirit without aromatics as no specific data indicate any clear neurotoxic differences between the different types.

6.1.5 Mutagenicity and Carcinogenicity

Mutagenicity

Based on a series of experimental data reported by WHO/IPCS (1996); SCOEL (2007) and OECD (2012) in vitro and *in vivo* data white spirit does not indicate further concern for mutagenic/carcinogenic effects. Thus white spirits have been tested with negatives results *in vitro* in bacteria, yeast and mammalian cells with and without metabolic activation. *In vivo* negative results were obtained in a dominant lethal inhalation study in rats; in mice and rat bone marrow mutagenicity assays and in a 3 months inhalation study with mice where the frequencies of micronucleated erythrocytes were examined (WHO/IPCS 1996; SCOEL 2007; OECD 2012).

Carcinogenicity

The carcinogenic properties of petrochemical products are usually ascribed to the content of benzene or polyaromatic hydrocarbons. In general the content of benzene in white spirit is very low and this is also controlled by the classification as white spirit with a content of benzene above 0.1% has to be classified as carcinogenic with Carc. 1B.

The International Agency for Research on Cancer, IARC in 1989 published an evaluation on the carcinogenic risk of occupational exposure to petroleum solvents, including white spirit (Group 3) and concluded that there is inadequate evidence for the carcinogenicity of petroleum solvents in humans. The limited epidemiological data available were inadequate to estimate the potential cancer risk of white spirit in humans (IARC, 1989).

After this a 2-year inhalation study with white spirit type 1 was carried out in rats and mice. Exposures were to 0, 138, 550, 1100 or 2200 mg/m³, 6 h/d, 5 d/w in rats and 0, 550, 1100 or 2200 mg/m³, 6 h/d, 5 d/w in mice.

In rats no neoplastic effect was observed in the females whereas increased incidences of adrenal medullary neoplasms occurred in males. In mice no neoplastic or non- neoplastic effect was observed in males whereas a significantly increase of multiple hepatocellular adenomas was found in females. Overall, the study concluded based on the significance of the findings at the various dose levels that there was some evidence of carcinogenic activity in male rats and equivocal evidence of carcinogenic activity in female mice (SCOEL 2007, NTP 2004).

These data that do not point to any consistent and conclusive picture with respect to carcinogenic effects may, however, as the data are not considered conclusive as to whether carcinogenicity should be an end-point of concern. Based on the negative data of mutagenicity of the substance it seems unlikely that the effects observed should be linked to any genotoxic effects of the substance which suggest a threshold level if possible carcinogenic effects should be considered.

Recently, IARC (2010) has concluded that there is sufficient evidence from data on painters that the occupation as a painter leads to increased risk for carcinogenic effects. Thus occupational exposure as a painter was placed in group 1 as carcinogenic to humans. It was recognized that painters have been or are exposed to a great variety of substances (a variety of solvents, metals and also asbestos) many of which are known as carcinogenic, so no specific exposure was identified as the overruling cause for the association. Thus in these cases no specific link to white spirit exposure can be made.

6.1.6 Reproductive and developmental toxicity

Three prenatal developmental toxicity studies have been identified with white spirit with aromatic content. In these studies rats were exposed by inhalation at dose levels in the range of 600 mg/m³ to 5700 mg/m³ at either day 6 to day 15 of gestation (two studies) or during day 3 to 20 of gestation (one study using only the dose level of 5700 mg/m³. In these studies no significant exposure related developmental findings were noted. At the highest dose level of 5700 mg/m³ the average foetal body weight was reduced and an increased incidence of delayed ossification and increased number of foetuses with extra ribs were noted, however, these findings were thought to be due to maternal toxicity at this dose level (WHO/IPCS 1996; SCOEL 2007; OECD 2012).

6.1.7 Dose-response estimation

According to SCOEL (2007), the NOAEL / LOAEL range for chronic neurotoxic effects after prolonged exposure of white spirit is in the range of 40 to 90 ppm. On this basis and after applying a safety factor of 2 SCOEL recommended an Occupational Exposure Level (OEL) of 116 mg/m³ (20 ppm) in order to prevent subtle chronic nervous system effects and organic brain damage as well to prevent acute irritation from eyes and respiratory tract. The OEL covered both white spirit with aromatic content as well as de-aromatized white spirit.

6.2 Human exposure

A major part of the manufactured white spirit is released to the air, owing to its use as a solvent and as the volatile ingredient in paints, varnishes and lacquers.

The components of white spirit do have different vapour pressure due to their chemical structure and molecular size, and therefore white spirit vapor does not have the same composition as the solvent. Both the gaseous phase and the liquid phase change during volatilization because of rapid evaporation of the most volatile components and slower evaporation of the less volatile ones. An exception to this is flash evaporation from a hot surface in which the total liquid phase is evaporated instantaneously. Thus the evaporation rate and the composition of the gaseous phase depend on temperature, air pressure, diffusion and convection properties. Aerosols formed during work will increase the surface area of the liquid and increase the evaporation rate (ECHA 2011b).

6.2.1 Direct exposure

6.2.1.1 Workers

NIOSH has made several surveys of white spirit (Stoddard solvent/mineral spirit) in various occupational environments. The following levels have been determined in samples taken in the breathing zone of workers: maintenance painters, 33-761 mg/m³ (NIOSH 1973); workers in airline hangars, 363-8860 mg/m³ (NIOSH, 1975a); workers inn screen cleaning processes, 137-385 mg/m³ (NIOSH, 1975b); workers at a washing machine for automobile parts, 43-594 mg/m³ (NIOSH, 1975c); manufacture of catapult cylinders, 2615 mg/m³ (spraying solvent), and up to 275 mg/m³ for painting operations (NIOSH, 1975d); ski boots finishing, 345-451 mg/m³ (NIOSH, 1975e); telephone cable assembly, 79-244 mg/m³ (NIOSH, 1980) from (all from WHO/IPCS 1996).

Overall, it is recognized that brush and roller application of alkyd paints leads to an average white spirit concentration of around 600 mg/m³ (100 ppm). Given that painters in the 1970-ties and 1980-ties were estimated to spend around 40% of their time applying alkyd paints (as opposed to applying water- based paints or preparing surfaces), an estimated average daily 8-hour exposure of 240 mg/m³ (40 ppm) has been used. It should be noted, however, that without ventilation, exposure can peak at much higher levels of between 1800 and 6000 mg/m³ (300 and 1000 ppm). Similar average and peak exposures have been reported in other industries, such as dry cleaning, where Stoddard solvent is used (WHO/IPCS 1996).

After these evaluations Caldwell et al. (2000) made an analysis of 99 publications (between 1961 and 1998) with a total of 16880 hydrocarbon solvent exposure measurements and compared these data to the respective TLV-values (threshold limit values = occupational limit values). The far highest exposure level for all the solvents was measured for white spirit/ Stoddard solvent which on the basis of 400 measurements had a weighted arithmetic mean exposure value of 466.5 mg/m³ which accounted for 89% of the TLV-value. On an overall basis the hydrocarbon exposure from the various solvents declined more than fourfold from the 70-ies up to the 90-ies.

No recent data on the representative occupational exposure levels of white spirit in Denmark has been found.

6.2.1.2 Consumers

The general population may be regularly exposed to white spirit, because of its extensive use in lacquers, paints and cleaning solvents. People who do home maintenance work or a lot of hobby work may be particularly exposed via inhalation of vapour or skin contact with the solvent. Exposure peak concentrations can be very high if there is a lack of occupational protection equipment, inadequate ventilation or little attention towards the possible danger of chemical exposure.

In general the same exposure levels for private use can be anticipated as the levels measured for workers under occupational conditions where average levels in the range of 470 mg/m³ to 600 mg/m³ and considerable higher peak levels have been found (see section below for worker exposure). However, the total life exposure from these activities will usually be much lower for consumers compared to workers occupationally exposed to white spirit.

A Danish EPA study in 1988 measured the exposure level in the inhalation zone during paint work done by brush in six different but realistic everyday scenarios. The conditions varied with respect to the painted area, ventilation, room volume, temperature, etc. The white spirit vapor levels in the different scenarios ranged from 270 to 6140 mg/m³ (Danish EPA 1988).

No further Danish EPA projects have specifically measured the various exposure scenarios that may occur from the use of different consumer product contain white spirit. However, two reports from the Danish EPA have identified white spirit as a constituent in products in consumer product surveys. In one survey white spirit was found in shoe polish at a content of up to 85% (Danish EPA 2005) and in another white spirit was found at a content of up to 60% in a product for polishing kitchen stoves (Danish EPA 2010b).

For shoe polish a worst case inhalation exposure scenario with a white spirit vapor concentration of 960 mg/m^3 was calculated, and a dermal exposure of 192 mg white spirit (100% absorption) was assumed (Danish EPA 2005).

For polishing metallic surfaces on kitchen stoves a worst case scenario with a white spirit vapor concentration of 150 mg/m^3 was derived, whereas skin exposure was not considered to contribute to the systemic exposure as no dermal uptake/absorption was expected (Danish EPA 2010b).

6.2.2 Indirect exposure

Indirect exposure to white spirit may occur after indoor use of paint or lacquers containing white spirit. The levels are considered considerable lower compared to direct consumer use of product containing white spirit.

Especially indoor air may contribute to indirect exposure due to e.g. evaporation from newly painted surfaces. However, due to the odour from the aromatic content of white sprit it can be assumed that the exposure will be kept at rather low levels by ventilating the rooms (odor threshold at $0.5-5 \text{ mg/m}^3$).

6.3 Bio-monitoring data

Measurements of hydrocarbons from white spirit exposure have been conducted in blood and other tissues in humans as well as in animals under experimental conditions in order to study the uptake, distribution and elimination of white spirit. The results based on these data are given in section 6.1. However, no surveys have been found where exposure of workers or a given population has been studied based on biomonitoring data on white spirit.

6.4 Human health impact

Workers

In the period 1978 to 1992 more than 5000 cases of chronic toxic encephalopathy due to long term exposure to organic solvents have been recognized as an occupational disease by the National Board of Industrial Injuries in Denmark. The number of cases peaked in 1987 with 574 cases. Today, however, this is a rarely diagnosed disease with 14 cases in the period of 2005 to 2009. This is mainly thought to be due to more controlled occupational uses of organic solvents but also to more stringent criteria for giving the diagnosis (Ingeniøren 1993, Sundhed.dk 2013).

The exposure values for e.g. the paint work given in section 6.2.1.1 and 6.2.1.2 above are in general higher than the current Danish occupational limit value of 145 mg/m³ and the recommended limit value by SCOEL of 116 mg/m³. In order to manage the potential risk and to protect workers from exposure to organic solvent including white spirit several regulatory measures and guidances have been introduced (see table 2-6.). Overall, work with white spirit and products with white spirit shall be organised to ensure the safety of the workers i.e. all unnecessary exposure should be avoided the use of local ventilation or closed spray boxes and use of protective equipment (gloves or respiratory protection) are to be carefully considered. Further substitution to less dangerous substances/ products always have to be considered by taking note of the labeling code of the products regarding the volatility and the hazardous effects of the product.

Consumers

For consumers only occasionally exposed to white spirit containing products (i.e. not on an everyday basis) the risk for organic toxic encephalopathy may be considered to be low or non-existent as this type of adverse effects do not develop until after many years of daily exposure.

However especially painting of indoor surfaces may generate high peak exposure up to about 6000 mg/m^3 and if consumers are not using adequate respiratory protection or ventilation this may lead to acute effects such as eye and respiratory tract irritation, dizziness, headache, nausea, tiredness and lack of coordination and extended response time.

6.5 Summary and conclusions

Human health hazards

The most critical effects with regard to human hazards are reflected in the classification used for the white spirit.

White spirit is subjected to EU harmonised classification with *Asp. Tox. 1; H304* (May be fatal if swallowed and enters airways) and in near future a classification with STOT *RE 1; H372 (Causes damage to the central nervous system through prolonged or repeated exposure)* will most probably be added as this classification has been concluded at ECHA.

Further the white spirit on the market is typically classified with:

Eye Irrit. 2: H319 (Causes serious eye irritation) and *STOT SE 3; H336* (May cause drowsiness or dizziness).

White spirit may be absorbed through inhalation of vapours and though skin contact to the liquid solvent (however to a lesser extent). After absorption white spirit is widely distributed throughout the body (brain, kidney, liver and fat), preferentially partitioning into fat; the half-life in adipose tissue has been estimated to be 46-48 hours. Thus accumulation of white spirit in fat tissue including the brain occurs when exposed daily. The distribution and accumulation in the brain is considered relevant for the adverse effects on the central nervous system.

Due to the low viscosity of the solvent white spirit may after oral ingestion be aspirated into the lungs and cause serious chemical inflammation and lung damage which may be fatal.

Acute central nervous system depression following acute inhalation exposure may lead to lack of coordination and extended response time. Further dizziness and tiredness may occur and exposure to very high concentrations of white spirit in enclosed spaces can in severe cases lead to narcotic effects and loss of consciousness. Further chest pain, cyanosis, apnea and cardiac arrest have been reported in severe cases.

The critical effects following repeated inhalation exposure to white spirit are the neurotoxic effects, which in humans after prolonged exposure may develop to chronic toxic encephalopathy. This has been documented in a series of occupational studies with painters conducted primarily in the Nordic countries in the 1970-ties and 1980-ties, where the exposure to white spirit were found to be associated to the reduced mental functioning and the symptoms from the central nervous system. These findings have recently been recognized at EU level in connection with agreement for the STOT RE1; H372 classification.

The NOAEL / LOAEL range for chronic neurotoxic effects after prolonged exposure of white spirit is in the range of 40 to 90 ppm. On this basis and after applying a safety factor of 2 the EU expert group, Scientific Committee on Occupational Exposure Limits (SCOEL) recommended an Occupational Exposure Level (OEL) of 116 mg/m³ (20 ppm) in order to prevent subtle chronic nervous system effects and organic brain damage. The OEL covers both white spirit with aromatic content as well as de-aromatised white spirit.

It is not possible to associate the adverse effects in the central nervous system to a specific hydrocarbon fraction in white spirit, so it remains unknown if the effects would also be associated to other types of hydrocarbon solvents than white spirit. So at present no marker for the neurotoxic effects can be identified with respect to single constituents or groups of constituents in the substances. On the other hand it is also not known whether the effects may be associated to the overall mixed chemical exposure from the white spirits. So at present the hydrocarbon mixture as

such reflected in these types of white spirit may be considered to be associated with the neurotoxicity of substances.

The content of the carcinogenic substance benzene in white spirit is controlled as classification with Carc. 1b has to apply if the content of benzene is above 0.1 w/w%. However, data from carcinogenicity studies with inhalation exposure to rats and mice were interpreted by the NTP as giving some evidence for carcinogenicity in rats and equivocal evidence in mice. These border line and inconsistent results need further expert evaluation in order to conclude whether the data suffice for a CLP Carc.2 classification.

The available experimental data on mutagenicity and reproductive toxicity do not indicate a further concern for these effects.

Exposure

Especially exposure to white spirit during painting operations have been studied, due to the widespread use of white spirit in paint. Overall, it is acknowledged that brush and roller application of alkyd paints leads to an average white spirit concentration of around 600 mg/m³ (100 ppm), but it should be noted that without ventilation, exposure can peak at much higher levels of between 1800 and 6000 mg/m³ (300 and 1000 ppm).

During polishing of metallic surfaces of stoves and during shoe polishing exposure estimates for white spirit of 150 mg/m^3 to 960 mg/m^3 have been made in two Danish surveys on consumer products where white spirit was found as a constituent. Exposure from dermal contact and absorption was estimated to be up to 192 mg per person per event from the stove polish. However proper data on the skin absorption of white spirit is missing.

Health impact

In Denmark the occurrence of organic toxic encephalopathy has decreased dramatically in relation to many years of focus on solvent exposure in the occupational environment and specifically on the focus on white spirit: In the period 1978 to 1992 more than 5000 cases of chronic toxic encephalopathy due to long term exposure to organic solvents have been recognized as an occupational disease by the National Board of Industrial Injuries in Denmark. Today, however, this is a rarely diagnosed disease with 14 cases in the period of 2005 to 2009.

For consumers only occasionally exposed to white spirit containing products (i.e. not on an everyday basis) the risk for organic toxic encephalopathy may be considered to be low to non-existent as this type of adverse effects do not develop until after many years of daily exposure.

However, especially painting of indoor surfaces may generate high peak exposure levels of up to about 6000 mg/m³ and if consumers are not using adequate respiratory protection or ventilation this may lead to acute effects such as dizziness, headache, nausea, tiredness and lack of coordination and extended response time.

7. Information on alternatives

Especially in the Nordic countries and including Denmark efforts have been made for several decades in order to reduce the exposure to organic solvents including white spirit based on the concern for the acute and chronic neurotoxic potential of the solvents.

This have been reflected in regulation and risk management measures undertaken by the authorities, which will be put further in perspective in this chapter regarding alternative substances and technologies.

In addition to this industry, worker organizations and also NGOs and the eco-labelling schemes play a very important and active rule in risk reduction by either promoting substitution of the use of white spirit or introducing measures for minimizing the exposure during occupational handling and use.

Below examples on the most important efforts and types of substitutions in relation to white spirit with aromatic content are given.

7.1 Identification of possible alternatives

7.1.1 Paint industry

After the second world war the old oil paint was replaced by alkyd paint because of easy available and rather cheap oil derived solvents such as white spirit. Thus in the 1960-ties alkyd paint were used all over in construction painting which further was reflected in very high exposures of construction painters towards white spirit. Due to the observation of neurotoxic effects among painters the Danish Painter´s Association in the 1960-ties and 1970-ties was the first to start working to achieve adequate risk management measures including substitution of the alkyd paints to water based paints. In 1986 surveys examining the toxicological properties and the occupational aspects of using water based paint were published. From these surveys it was concluded that the use of water based paints had clear occupational advantages compared to the use of alkyd paints. This and other regulatory initiatives lead to an overall substitution of alkyd paint use professionally and in 1990 it was estimated that water based paint accounted for 90% of all paint used for construction painting (Danish Painter´s Association 1990).

This substitution towards use of water based paints is confirmed by the Danish paint and lacquer industry that states that the use of paints by consumers and by professionals to day totally is dominated by the use of water based paint and lacquers (DFL 2013, personal communication).

The search for alternatives for white spirit in paints is ongoing, and recently a new technology using nanoparticles of silica has been developed for use in products for outdoor wood protection where it has been difficult to substitute to water based paint with same performance as the white spirit based paints. According to a recent publication this new formulation is based on fewer and less hazardous ingredients compared to the conventional products for wood protection, and the products which are not to be classified as hazardous comply with the criteria for obtaining the Nordic Swan and the EU-flower eco-labeling (Danish EPA 2012). In the Danish metal industry substitution to water based paints has only been possible to a minor extent due to lower technical performance of the water

based paints. In 1988 the use of paints in the metal industry was divided as follows (Danish EPA 1990):

- Conventional solvent based paints: 70%
- Water based paints: 10%
- Powder paints: 20%

In connection with high technical performance the Danish paint and lacquer industry confirms that substitution may not always be possible, although efforts towards substitution to water based paints, UV-paints and high solid paints has been undertaken (DI 2013, personal communication). However, no quantitative information was available on this development.

7.1.2 Wood impregnation

In vacuum impregnation (in contradiction to high pressure impregnation) of wood the use of white spirit cannot be substituted by water in the wet impregnation process where white spirit is the main constituent in the impregnation solvent. Vacuum impregnation of wood has to be conducted on plants approved by the Danish Impregnation Inspection and due to strict standards and new technology the use of impregnation solvent has decreased from 125 kg per m³ wood in 1970 to 26 kg per m³ wood in 2000.

Further measures are available for either recycling white spirit (condensation) or removal of vapours from the emitted air by use of active carbon filters or burning after concentration of the emitted vapours (Danish EPA 2000).

7.1.3 Printing Industry

In the printing industry large efforts have been made towards identifying cleaner technology and alternatives to dangerous substances including white spirit as described by Danish EPA (1995) and NCM (1998) and as indicated below.

Traditionally hydrocarbon solvents and especially white spirit have been used heavily for cleaning of printing machines and printing equipment. Thus for the printing industry in Sweden a consumption of approximately 1000 t of organic solvents was estimated in 1994 of which 60-90% was anticipated to evaporate and emitted into the air. This indicates concern for occupational health as well for the environment with regard to VOC emissions.

This heavy use of organic solvent/ white spirit may according to NCM (1998) be avoided by the development of alternative technologies e.g. use of UV- curing colors, colors with high content of dry matter, water based colors, and digital printing.

For cleaning in the printing industry a shift has been made from white spirit to refined plant oils which now, however, has further shifted to the use of monoesters of fatty acids from plant oil due to better technical performance of these second generation cleaners. Already in 1996 the share of VCA cleaning (vegetable cleaning agents) compared to the use of organic solvents were about 40% in the Danish printing industry.

From the 1970-ties up to 1990 several occupational cases of chronic neurotoxicity were seen in the printing industry due to the use of organic solvents. Due to awareness and shift towards alternative substances and new technology (as indicated above) this has improved dramatically. Here the reduced amount of organic solvent is considered the main cause even though organic solvents still are used in reduced amounts for some types of printing (Schultzer 2008).

7.1.4 Other examples: cleaning, degreasing, corrosion inhibition

At the web site for Ecolabeling Denmark (<u>http://www.ecolabel.dk</u>) a substitution of white spirit towards a mixture of plant oil (canola oil) and animal fat (sheep visceral fat) is described. The product containing this mixture can be used for removal of paint and coal tar including cleaning of paint equipment.

At the CatSub website (<u>www.catsub.dk</u>) the following examples of substitution were retrieved:

Solvents containing white spirit were used for cleaning machines and part of machines. The solvents were substituted with success with a product containing an ester derived from fatty acids from coconut oil.

Solvents containing 70% white spirit was used for corrosion inhibition of tools but where substituted to a mixture of mineral oil and oil additives

White spirit based bitumen products for surface treatment of roads and bicycle paths were successfully substituted with bitumen products containing 30% and 1% emulsifiers or bitumen in plant oil.

At the Danish EPA consumer website it is recommended to use soft soap instead of organic solvents/white spirit for paint removal and for cleaning brushes and other paint equipment. (http://www.mst.dk/Borger/Temaer/Gor_det_selv/Maling+og+lak/)

The use of soap, plant oil and esters of plant oils are examples of introducing alternative substances with very low volatility and low hazard potential as well in terms of human health and environment.

Thus, today industry sees a great potential for substituting organic solvents/ white spirit in products categories covering: cold cleaners, automotive cleaners, and industrial degreasers (Estichem 2013, personal communication)

7.1.5 Other hydrocarbons e.g. dearomatised white spirit (type 3)

As shown in section 3.4 the use of the dearomatised white spirit (white spirit type 3) has during the last decade increased from a tonnage level about 4 times below the traditional white spirit to a tonnage level 3-4 times above today.

Of the tonnage level of 12,382 tonnes today the uses are split in the following product categories (From Danish Product Registry 2013):

Solvent and thinners:	4,725 tonnes
Paint and lacquers:	1,275 tonnes
Cleaning/washing agents:	1,018 tonnes
Adhesives binding agents:	647 tonnes
Corrosion inhibition:	339 tOnnes
Reprographic agents:	261 tonnes
Fuels:	212 tonnes
Non-agricultural pesticides	
And preservatives:	111 tonnes
Surface-active agents:	103 tonnes

(In 2009 and 2010 there was a very high annual consumption of white spirit type 3 at a total level of about 65,000 tonnes, however, the additional volumes used in these years were for corrosion inhibition).

Thus the uses of white spirits type 3 are very much the same as for the traditional white spirit, so the decrease in use of traditional white spirit and the increase of the use of white spirit type 3 indicates a substitution towards the use of white spirit type 3.

The advantage of using white spirit type 3 is its less intense odour compared to white spirit with aromatic content whereas it is difficult to discriminate between the toxicological properties of white spirit type 3 (no aromatics) and white spirit with aromatic content.

In fact white spirit type 3 was included in the proposal from Danish EPA when they put forward the classification proposal for white spirit for STOT RE1 proposal, as both WHO/IPCS 1996 and SCOEL (2007) concluded that the neurotoxic potential for white spirit type 3 should be considered the same as for the other white spirits with aromatic content. However, the RAC committee did not accept this proposal due to lack of specific data on the specific substance.

Thus no clear toxicological advantage can be concluded when substituting to white spirit type 3 unless the vapour pressure of the white spirit type 3 is lower compared to the 'old' white spirit as this of course will reduce the inhalational exposure potential of the solvent.

Due to the harmonised EU classification as STOT RE1 has been adopted for white spirit type 0, white spirit type 1 and Stoddard solvent it may be anticipated that there may be as shift towards use of closely related hydrocarbon solvents including white spirit type 3, that does not have a harmonised classification. A preferred substitution would be towards solvents with lower vapour pressure in order to reduce inhalational exposure of hydrocarbon vapors and the risk for adverse neurotoxic effects.

Typical candidates for substitution would be other hydrocarbon solvents in the HSPA category C9-C14 aliphatics (2-25% aromatics) and C9-C14 aliphatics ($\leq 2\%$ aromatics).

7.2 Drivers for substitution

7.2.1 Regulation with additional product labeling

The development of the volatility code in 1968 is considered the most important tool for substitution of white spirit into water based product and less volatile solvents (Danish Painter´s Association (1990). The code that has to be attached to the products is linked to specific occupational measures to be implemented by professional users as well as it restricts the marketing of products directed towards private consumer use, see table 2-5 concerning regulation.

Also the use of the EU safety clause and the national application of classification with R48/20 for white spirit as described in section 2 has been an important driver for the Danish efforts for substituting white spirit in products.

7.2.2 Ecolabelling

As described in table 2-6 ecolabelling schemes have rather strict criteria for the use of VOCs and the use of substances classified in specific hazard categories e.g. STOT RE1 and Aquatic Chronic 2. This to a great extent limits the use of white spirit type 0, white spirit type1 and Stoddard solvent in an ecolabelled product. Thus, for product groups such as indoor and outdoor paint and varnishes, car and boat care products and cleaning products the criteria towards the content of VOCs, aromatic hydrocarbons and substances classified as STOT RE1, would make it nearly impossible to use white spirit and obtain the ecolabel at the same time.

7.3 Historical and future trends

As indicated above the present regulation and also the ecolabelling system put a continuous pressure on the efforts in substituting white spirit or to introduce adequate risk management measures in situations and processes where substitution cannot be undertaken due to lack of alternatives.

As it has happened for professional products this trend may also be reflected in the future in the use of consumer products.

Thus it may be anticipated that in the future and especially when the harmonised classification as STOT RE1 of white spirit is implemented at EU level the use volume of white spirit with aromatic content may further decline.

7.4 Summary and conclusions

Many years focus on the use of white spirit (since the 1960-ties) has created a process where large efforts have been made by labor organizations, authorities, NGOs and industry in order to find alternatives for the use of white spirit.

For the paint industry this has led to an overall shift from the use of white spirit based paint to water based paint for construction painting both for professional products as well as for consumer products. A similar trend has been observed in the printing industry where the use of white spirit has declined dramatically due to new technologies and use of alternatives products primarily based on plant oils and mono-esters of plant oil fatty acids.

There seems to be a further potential for substitution especially for cleaning purposes termed as: cold cleaners, automotive cleaners, and industrial degreasers where the use of mono-esters of fatty acids derived from plant oil may take over.

However, there are still areas where the substitution of white spirit containing product is difficult or impossible e.g. surface treatment or painting of metals and in vacuum impregnation of wood.

Substitution to other comparable hydrocarbon solvents should be undertaken with care as the toxicological properties of these solvents appear to be similar, although the available data are not sufficient for a harmonised classification. However, reduction of the risk potential for adverse effects may be gained if the substituting solvent has a lower vapor pressure and thus poses a lower potential for inhalation of vapours.

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Appendix 1

	Aromatic containing White Spirits					
White Spirit type	New Solvent identified by new HSPA naming	new EC number	registration number	Old iden EINECS no	tification by CAS no	
White Spirit type 0	Hydrocarbons, C9-C12, n-alkanes, isoalkanes, cyclics, aromatics (2-25%)	919-446-0	01-2119458049-33	265-191-7	64742-88-7	
White Spirit type 1	Hydrocarbons, C8-C12, n-alkanes, isoalkanes, cyclics, aromatics (2-25%)	928-136-4 927-344-2	01-2119484809-19 01-2119463586-28		64742-82-1 64742-82-1	
Low flash point	Hydrocarbons, C9-C10, n-alkanes, isoalkanes, cyclics, aromatics (2-25%)					
Medium flash point	Hydrocarbons, C9-C12, n-alkanes, isoalkanes, cyclics, aromatics (2-25%)	919-446-0	01-2119458049-33	265-185-4 232-489-3	64742-82-1 8052-41-3	
High flash point	Hydrocarbons, C10-C13, n-alkanes, isoalkanes, cyclics, aromatics (2-25%)	919-164-8	01-2119473977-17	265-185-4 232-489-3	64742-82-1 8052-41-3	

White spirit according to the new HSPA naming system

(source: HSPA (2011b). Definition of White Spirits under RAC Evaluation Based on New Identification Developed for REACH).

Appendix 2

Chemical constituents in white spirit

Content of aliphatic and cyclic alkanes in white spirit (WHO/IPCS, 1996)

Molecular size	North European white spirit ^a		USA white spirit (Stoddard solvent) ^D			
	Alkanes (% w/w) ^c	Monocyclic alkanes (% w/w)	Dicyclic alkanes (% w/w)	Alkanes (% v/v)	Monocyclic alkanes (% v/v)	Dicyclic alkanes (% v/v)
C ₆	-	0.01	-	-	-	-
C7	0.10 (0.064)	0.17	-	-	2.4	-
C8	0.88 (0.58)	1.4	-	0.9	4.3	-
C9	10 (7.4)	8.7	1.7	9.5	5.0	2.7
C ₁₀	17 (11)	11	3.5	21	8.4	4.7
C ₁₁	8.4 (4.0)	3.8	3.2	13	6.0	3.2
C ₁₂	0.58 (0.58)	0.65	0.46	3.4	1.0	1.0
C6-C12	37 (23)	26	8.9	48	26	12
C ₆ -C ₁₂	total alkanes: 729	% specified (+ 12%	unspecified)	total alkanes: 8	5%	

^a Varnolene (boiling range: 162-198 °C), white spirit from the Danish market ^b Stoddard solvent (boiling range: 152-194 °C), white spirit from the USA market ^c The values in parentheses indicate the percentage by weight of n-alkanes

Table 2. Content of aromatics in white spirit (WHO/IPCS, 1996)

Molecular size	Substance	North European white spirit ^a (% w/w)	USA white spirit (Stoddard solvent) ^b (% v/v)
C6	Benzene	0.001	0.1
C7	Toluene	0.005	0.4
C8	Ethylbenzene o-xylene m-xylene p-xylene total C8 aromatic hydrocarbons	0.2 0.34 0.49 0.22 1.3	1.4
C9	n-propylbenzene isopropylbenzene (cumene) 1-methyl-2-ethylbenzene	0.97 0.21 0.60	
	1-methyl-3-ethylbenzene 1-methyl-4-ethylbenzene 1,2,3-trimethylbenzene (henimellitene)	1.2 0.66 0.62	
	1,2,4-trimethylbenzene (pseudocumene) 1,3,5-trimethylbenzene (mesitylene) trans-1-propenylbenzene total C9 aromatic hydrocarbons	2.1 0.83 0.40 7.6	7.6

C ₁₀	n-butylbenzene	0.97		
10	isobutylbenzene	0.37		
	sec-butylbenzene	-		
	tert-butylbenzene	-		
	1-methyl-2-isopropylbenzene (o-cymene)	0.06		
	1-methyl-3-isopropylbenzene (m-cymene)	0.47		
	1-methyl-4-isopropylbenzene (p-cymene)	0.62		
	1,2-diethylbenzene	0.13		
	1,3-diethylbenzene	0.25		
	1,4-diethylbenzene	0.13		
	1,2-dimethyl-3-ethylbenzene	0.08		
	1,2-dimethyl-4-ethylbenzene	0.25		
	1,3-dimethyl-2-ethylbenzene	-		
	1,3-dimethyl-4-ethylbenzene	0.26		
	1,3-dimethyl-5-ethylbenzene	0.38		
	1,4-dimethyl-2-ethylbenzene	0.28		
	1,2,3,4-tetramethylbenzene (prebnitene)	0.16		
	1,2,3,5-tetramethylbenzene (isodurene)	0.14		
	1,2,4,5-tetramethylbenzene (durene)	0.34		
	tetralin	0.08		
	total C10 aromatic hydrocarbons	5.2		
			3.7	
C11	total C11 aromatic hydrocarbons	1.2	0.9	
C ₁₁		1.2	0.9	
C12	total C12 aromatic hydrocarbons	0.12	0.1	
-	indans + tetralins		0.5	
C6-C12	total aromatic hydrocarbons	15.4	14.7	

^a Varnolene (boiling range: 162-198 °C), white spirit from the Danish market ^b Stoddard solvent (boiling range: 152-194 °C), white spirit from the USA market

Appendix 3

Background information to chapter 3 on legal framework

EU and Danish legislation

Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- <u>Regulations</u> (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- <u>Directives</u> (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvering as to the form and means of implementation. However, there are great differences in the space for manoeuvering between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- <u>Decisions</u> are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.
- <u>Recommendations and opinions</u> are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulate to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation REACH and CLP

The REACH Regulation¹ and the CLP Regulation² are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

¹ Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

² Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

(Pre-)Registration

All manufacturers and importers of chemical substance > 1 tonnes/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered dead-lines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

Evaluation

A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation

Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction

If the authorities assess that that there is a risk to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling

The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publish the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

On-going activities - pipeline

In addition to listing substance already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)

The EU member states have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV

Before a substance is included in REACH Annex XIV and thus being subject to Authorisation, it has to go through the following steps:

- 1. It has to be identified as a SVHC leading to inclusion in the candidate list3
- 2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
- 3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions

When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

•

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intensions in relation to Annex XV dossiers divided into:

- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions
- •

for the three types of Annex XV dossiers.

International agreements

OSPAR Convention

OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

 $^{^{3}}$ It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by <u>other agreements</u> setting out:

- issues of importance
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out.
- guidelines or guidance setting out the way that any programme or measure should be implemented
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

HELCOM - Helsinki Convention

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the <u>Helsinki Convention</u>.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

Stockholm Convention on Persistent Organic Pollutants (POPs)

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention

The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as "hazardous wastes" based on their origin and/or composition and their characteristics, as well as two types of wastes defined as "other wastes" - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

Eco-labels

Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower

The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

Nordic Swan

The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" (http://www.ecolabel.dk/). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).

Blue Angel (Blauer Engel)

The Blue Angel is a national German eco-label. More information can be found on: <u>http://www.blauer-engel.de/en</u>.

Appendix 4

Epidemiological studies on workers predominantly exposed to white spirit and dose-response related findings (data from WHO/IPCS 1996 and SCOEL 2007, compiled in ECHA 2011a)

Reference/type of study	Groups studied	Exposure	Results
Lindström and Wickström (1983) Cross-sectional study. Questionnaire and 8 neuropsychological tests determining intelligence and psychomotor performance	219 housepainters and 229 reinforcement workers	The mean exposure period was 22 years with an estimated average level of white spirit of 40 ppm (232 mg/m ³) during working hours; exposure indices made for total life-time exposure and average exposure levels	Among painters, there were significantly increased prevalence of acute symptoms such as nausea, runny noses and malaise, and significantly poorer performance in 4 tests. Short-term visual memory and simple reaction time were most affected functions. For these functions, a slight correlation between performance and total expo- sure/exposure level was demonstrated.
Fidler et al. (1987), Cross-sectional study. Questionnaire Neuropsychological tests (8 tests for intellectual functions and psychomotor performance).	101 construction painters and 31 dry wall tapers (the control group was not used in the evaluation because of pronounced differences compared to the painter group)	The painters were exposed to mixed solvents. Exposure indices were calculated on the basis of duration of exposure (years as a painter), type of work, frequency of expo- sure, amount of solvent used, exposure during the latest year, etc. The mean exposure period was 18 years.	Among painters, dose-related increase in symptoms such as dizziness, nausea, fa- tigue, feeling of drunkenness and mood tensions were observed. Impaired perform- ance in one psychomotor performance test and in one short-term memory test was associated with the exposure during the latest year. Because signs of mental im- pairment did not form a consistent pattern the findings in the study were judged to be in accordance with the WHO definition of the mildest form of chronic solvent toxicity.

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Baker et al. (1988) Cross-sectional study Questionnaire Neuropsychological test battery (9 tests determining verbal ability, psychomotor performance and memory).	186 construction painters	Information about intensity and duration were combined and different exposure indices were calculated. Stratification to 6 sub- groups, according to the index of lifetime exposure intensity (LEI), was done. The mean exposure period was 12 years.	Unadjusted as well as adjusted (adjust- ments were made by regression analysis to account for the factors age, race, educa- tion, social status and alcohol habits) prevalence rates of symptoms such as forgetfulness, lassitude, disorientation, dysphoria and numbness of fingers and
			toes increased significantly with increasing LEI. Significant dose (LEI)-response rela- tionship was also found for five mood pa- rameters and in the symbol-digit test. When stratifying according to exposure duration without accounting for the exposure intensity, the neuropsychological parameters were affected to a minor degree.
Mikkelsen et al. (1988) Cross-sectional study Neuro- psychological test battery (13 tests intellectual functions and psychomotor performance), by neurological tests (motor performance, coordination, re- flexes, sensitivity) and by neu- rophysiological examination (CT).	85 painters and 85 bricklayers	White spirit was estimated to account for about 75% of the total solvent exposure. The mean exposure period was 32.5 years with an average daily solvent consumption of 1.3 $l/d = 41.4$ (l/d) years. Solvent exposure was graded according to the cumulative solvent consumption. Low exp.: < 15 (l/d) years (n=22); medium exp.: 15-30 (l/d) years (n=29); high exp.: > 30 (l/d) years (n=33). Average exposure level (all painters) was estimated to be 40 ppm. Twenty-one painters had been exposed during the latest week before examination.	The following odds ratios (OR) for painters compared to bricklayers were found for the development of dementia (the presence and degree of dementia evaluated from the overall performance in the test battery): high exp.: OR= 5.0 (p < 0.05); medium exp.: OR= 3.6 (p < 0.05); low exp.: OR= 1.1. Only a weak correlation was found between exposure and performance in specific neurological tests. However a strong correlation was found between exposure levels and the total number of abnormal scores. In CT scanning, exposure and dose relationship for differences were noted in 3 out of 11 different parameters. An average no- observed-effect level of 40 ppm (232

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			mg/m ³) for 13 years was estimated (possible confounders were identified and taken into account).
Bove et al. (1989) Cross-sectional study Vibration thresholds and tem- perature sensitivity.	93 construction painters and 105 unexposed controls	Mixed solvents with a mean exposure period of 18 years. Different exposure indices were calculated on the basis of intensity and duration of exposure.	The vibration thresholds were significantly higher in the older painters than in the comparable controls. The painter group had a significant excess of high-level temperature sensitivity compared to controls. Among painters, there was a positive association between vibration threshold and exposure level and cumulative exposure over the past year.
Bazylewicz-Walczak et al. (1990) Cross-sectional study Neuro-	226 rubber footwear industry workers and 102 non-exposed hosiery plant workers	Solely white spirit exposure from gluing. The mean exposure period was about 500 mg/m ³ in the last 13 years. The two groups were divided into	The performance of the exposed groups (as a total), compared to the controls, was significantly worse with regard to 4 of the 7 tests for intellectual functioning and with
psychological test battery (7 tests for intellectual functions and 5 tests for psychomotor performance).		three sub-groups with respect to age. Further the exposed subjects were divided according to exposure duration: I: 5-10 years (n=51); II: 11-15 years (n=103); III: 16-30 years (n=72).	regard to 3 of the 5 tests for psychomotor performance. The affected variables were: correctness of perception and reproduction of visual material, projection of spatial rela- tionships, concentration, speed of reactions to single and complex light stimuli, and manual dexterity. Variables such as simple and complex reaction time and coordination were found to deteriorate with duration of exposure.
Spurgeon et al. (1990,1992) Cross-sectional study. Questionnaire concerning symptomatology and psychiatric state Neuropsychological test battery for intellectual functions and perceptual speed.	Study group 1: 90 brush painters and 90 unexposed age- matched controls. Study group 2: 144 solvent-exposed brush painters, spray	Study group 1: Mainly exposed to white spirit with an estimated average level of 50 ppm for 2 days a week. Study group 2: Exposure more diverse because of the inclusion of several different occupations. Both groups were divided into four subgroups of exposure duration: < 10 years, 10-20 years, 21-	In both studies, significantly impaired performance was observed in the symbol- digit substitution test for the exposed groups. In study 2, the performance of workers exposed for more than 10 years

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	painters, printers and others, and 144 unexposed age- matched controls.	30 years, > 30 years.	was worse in paired associate learning test. After accounting for other possible influences on performance, a significant effect from exposure remained only for the sub-groups exposed for more than 30 years. It was concluded that the investigation provided some evidence for effects on cognitive functioning after long- term solvent exposure.
Bolla et al. (1995), Ford et al. (1991) Cross-sectional study Neuro- psychological test battery.	 144 workers from two paint- manufacturing plants (from same exposure group as Bolla et al. (1990) and Bleecker et al. (1991)) 52 unexposed workers 	At both plants, aliphatic hydrocarbon mixtures (white spirits), toluene and xylene were the three most widely used solvents. The cumulative hydrocarbon exposure was 180 ppm x years and 97 ppm x years at the two plants, respectively. Lifetime-weighted aver- age exposure was 11.7 ppm and 7.6 ppm, respectively.	The performance of the exposed group was worse in 14 out of 15 test parameters. Significantly impaired performance was noted in 5 tests for motor function and manual dexterity. In 10 out of the 15 tests, there was a positive trend between impaired performance and duration of exposure (for 3 tests $p < 0.05$). The scorings were adjusted for the cofactors age, vocabulary and race.
Lundberg et al. (1995) Cross-sectional study Neuropsychological test battery, 12 psychometric tests	135 house painters and 71 house carpenters, affiliated with their respective trade unions for at least 10 years before 1970	In the latter part of the 1950s and in the 1960s, white spirit was the dominating solvent in alkyd-based paints. Their lifetime organic solvent exposure was evaluated through the aid of an interview	Neuropsychiatric symptoms compatible with chronic toxic encephalopathy were more common among the painters than among the carpenters, and these symp- toms became increasingly prevalent with increasing cumulative solvent exposure. Nevertheless, Profile of Mood State was not different. In the block design test, one of the 12 used psychometric tests, the painters performed worse than the carpen- ters and the painters' performance de- creased with increasing cumulative expo- sure. In the majority of the psychometric

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			tests, the painters with low exposure tended to show better and heavily exposed painters worse results than the carpenters. The 52 painters with the heaviest cumula- tive exposures and 45 carpenters were examined for psychiatric diagnosis, with electroencephalography and auditory evoked potential. These three investiga- tions showed no difference between the painters and the carpenters. The authors considered that the symptoms were caus- ally related to the solvent exposures and that the cumulative exposure to solvents below 130 exposure-limit months does not lead to functionally lasting disturbance of the nervous system. An exposure of about 130 to 250 exposure-limit months was related to an elevated risk of symptoms associated with chronic toxic encephalopathy and showed an indication of effects on one psychometric test, which, however, may have been confounded by recent exposure. The 130 exposure-month can roughly be estimated to no higher than 540 mg/m ³ (approximately 90 ppm), assuming the shortest exposure period of 10 years (120 exposure-months).

Survey of white spirit

This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The report includes an introduction of 3 white spirits and presents available information on the use and occurrence of the substances internationally and in Denmark and on legislation concerning white spirit. It compiles information on environmental and health effects, on waste management and on alternatives to the substances.

Kortlægning af mineralsk terpentin

Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Ud fra tilgængelig viden indeholder rapporten en introduktion til 3 mineralske terpentiner og indeholder blandt andet en beskrivelse af brugen og forekomsten af mineralsk terpentin internationalt og i Danmark og om lovgivningen der er relevant for stoffet. Rapporten sammenfatter viden om miljø- og sundhedseffekter af mineralsk terpentin, om affaldsbehandling og om alternativer til stofferne.



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