POTENTIAL RISKS OF HYDROGEN SULPHIDE THROUGH THE BITUMEN MANUFACTURE AND DELIVERY PROCESS

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1. BACKGROUND

Hydrogen sulphide (H_2S) is naturally present in crude oils and can be formed during the refining process and in storage tanks downstream of the refinery. Although the presence of H_2S in bitumen liquid phase is not always identified, the gas can still be present and can accumulate in enclosed spaces during hot storage or transport. In the event of prolonged storage, especially at high temperature, the headspace of storage and truck tanks can contain significant amounts of hydrogen sulphide that may reach dangerous concentrations.

2. SCOPE

The objective of this report is to raise awareness of all people involved through the bitumen supply chain (i.e. staff and management of refineries, bitumen depots, bituminous binder plants, asphalt plants, bitumen roofing industry, hauliers, etc...) of risks related to the handling of bitumen associated with the presence of H_2S in the vapour phase of bitumen and the importance to limit personal exposure to H_2S.

The scope of this report is to describe the risk for selected operations and provide general recommendations on how to manage the associated risks. The review covers storage, transfer, loading, transport and discharge of bituminous binders in refineries, depots, polymer modified binder manufacturing facilities and customer sites. This document covers all types of bitumen, including; conventional bitumen grades, oxidised bitumen and polymer modified bitumen (PmB). It does not include the manufacture, storage, transport or application of asphalt mixtures.

It is recognised that various measures may be taken during the manufacture of bitumen to reduce the quantity of hydrogen sulphide potentially present. These may include stripping (driving off the molecules with another gas), use of additives (neutralisation of hydrogen sulphide), or degasification in storage (the gas dissolved in the bitumen naturally tends to escape from the liquid mass over the course of time). The use of such techniques to reduce the hazard and risk from H_2S in bitumen is not covered in this report.

3. HYDROGEN SULPHIDE (H_2S) AND ASSOCIATED HEALTH HAZARDS

H_2S is a gas that can be released from hot bitumen. It is probably best known for its recognisable "rotten eggs" smell that is detectable in very low concentrations.

Hydrogen sulphide:

- Is toxic, acting on the nervous system
- Can deaden the sense of smell, so odour is not a reliable way to detect its presence
- Is highly flammable
- Can react with iron oxide (rust) on the walls and ceilings of tanks to form pyrophoric iron sulphide, a known ignition source in the presence of oxygen

Bitumen manufacturers should ensure that hazards associated with their products are adequately communicated to customers, together with risk reduction measures. This information is included in Safety Data Sheets (SDS).

Table 1. Typical physiological responses/effects following exposure to a range of concentrations of hydrogen sulphide (H_2S) [based upon World Health Organisation, CICAD 53[A]]

Exposure (mg/m^3)	Effect / observation	Reference
0.011	Odour threshold	Amoore & Hautala, 1983[2]
2.8	Bronchial constriction in asthmatic individuals	Jappinen et al., 1990[3]
5.0	Increased eye complaints	Vanhoorne et al., 1995[4]
7	8 hour Time Weighted Average Occupational Exposure Limit	Scientific Committee on Occupational Exposure Limits (SCOEL)
14	Short-Term Exposure Limit	SCOEL
5–29	Eye irritation	IPCS, 1981[5]
28	Fatigue, loss of appetite, headache, irritability, poor memory, dizziness	Ahlhorg, 1951[6]
139	Immediately Dangerous to Life and Health (IDLH)	NIOSH[7]
>140	Olfactory paralysis (Sense of smell cannot be relied upon to detect H_2S)	Hirsch & Zavala, 1999[8]
>560	Respiratory distress (breathing difficulty)	Spolyar, 1951[9]
≥700	Death	Beauchamp et al., 1984[10]

Occupational Exposure Limits (OELs) typically represent the time-weighted average (TWA) exposure concentration of a toxic substance permitted over an 8-hour working day and a 40-hour working week. They represent a concentration to which most workers may be repeatedly exposed, day after day, without significant adverse health effects. In the case of hydrogen sulphide, the limit is primarily based on avoiding transient sensory irritation in the eyes, nose, and throat.

[A] 2009/161/EU of 17 December 2009 establishing a third list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Commission Directive 2000/39/EC

OELs are intended to protect most of the working population from adverse health effects but some exceptions may occur with unusually sensitive individuals. For some substances, as is the case for H_2S, brief exposures to high vapour concentrations may cause localised irritation that require establishing Short-Term Exposure Limits (STELs). STELs typically represent a 15-minute TWA concentration that should not be exceeded. The IDLH was considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection should be permitted. In determining IDLH values, NIOSH considered the ability of a worker to escape without loss of life or irreversible health effects along with certain transient effects, such as severe eye or respiratory irritation, disorientation, and incoordination, which could prevent escape. As a safety margin, IDLH values are based on effects that might occur as a consequence of a 30-minute exposure. However, the 30-minute period was NOT meant to imply that workers should stay in the work environment any longer than necessary.

The Commission Directive 2009/161/EU[A] establishes a third list of Community Indicative Occupational Exposure Limit Values (IOELVs) for the protection of workers from chemical risks, to be set at Community level. IOELVs are health-based, non-binding values. Hydrogen sulphide is included in this Directive, which means that, Member States are required to establish a national occupational exposure limit value taking into account the Community limit value, but may determine its nature in accordance with national legislation and practice. The IOELV for H_2S are:

- TWA (8h): 5 ppm (7 mg/m^3)
- STEL (15 min): 10 ppm (14 mg/m^3)

A list of organisations who set national regulations for H_2S is given in Appendix 1.

4. EVALUATION OF RISKS

Eurobitume has collected H_2S concentration data from its members. The data collected shows significant variation in H_2S concentrations, which could be explained by various factors including:

- Variation in measurement techniques and sampling protocols (which can vary in accuracy and can be affected by interference from other, non-H_2S, compounds present in the atmosphere)
- Measurements taken at variable distances from the H_2S source. Where distance from the source vs personal exposure measurements were recorded, it indicated that the concentrations of H_2S decreased rapidly over increasing distance from the source
- Variability of local conditions at the time of the measurements e.g. temperature, wind direction, precipitation etc...

These data are not sufficient to give a robust assessment of risk but show that the concentration of H_2S in gas phase can reach dangerous or lethal levels in the headspace of the truck trailer or storage tank headspaces. Consequently, the potential for exposure to significant amounts of hydrogen sulphide is greatest during operations associated with headspace of heated storage tanks and delivery trucks and in activities close to the manhole and ventilation outlets. Therefore, the possibility exists for extremely high exposures in a very short period, even if the short- and long-term OELs are not exceeded. Caution should be taken when opening man lids and where drivers / operators could be in closer proximity to the source of high H_2S concentrations.

5. RISK MANAGEMENT THROUGH THE BITUMEN SUPPLY CHAIN

Directive 89/391/EEC[B] places an obligation on employers to "take the measures necessary for the safety and health protection of workers, including prevention of occupational risks and provision of information and training". It is therefore the responsibility of all employers to ensure that employees and other workers on a worksite are aware of the hazards that may be present and that risk management measures are developed to ensure that workers are not exposed to unacceptable risks while carrying out their duties.

Normal operations in open or well-ventilated areas are unlikely to present serious hazards from H_2S during bitumen operations. However, since bitumen may contain H_2S, normal operations of loading/unloading, tank sampling and any activities close to manholes or ventilation pipes should take the potential presence of H_2S into account and employers should carry out a comprehensive risk assessment taking into consideration the following items. The risk assessment should include risks facing specific types of workers and decide on the protective measures to be taken and, if necessary, the protective equipment to be used.

5.1. Identification of areas

Instances, circumstances and locations where contact with hydrogen sulphide may occur should be clearly identified. A specific identification could be added if concentrations are immediately dangerous to life or health (IDLH)[C] ; A level of atmospheric concentration that poses an immediate threat to life, or would cause irreversible or delayed adverse health effects, or would interfere with an individual's ability to escape from a dangerous atmosphere, e.g. flow-charts.

5.2. Warnings

Warnings should be provided for areas where there is a risk of hazardous concentrations of H_2S e.g. warning signs at storage tanks, loading sites, etc...

In addition, systems that monitor for hydrogen sulphide (e.g. personal gas detection, hand-held gas detectors, fixed gas detection systems) are recommended to assess concentrations in areas where H_2S may reach hazardous concentrations.

5.3. Loading facilities and ventilation

For areas where there is a risk of hazardous concentrations of H_2S, either natural or forced (e.g. local exhaust) adequate ventilation should be provided.

In order to minimize the potential for breathing dangerous levels of H_2S, where possible operators and drivers should position themselves "upwind" when opening manholes or access hatches.

5.4. Temperature management

Temperature is one of the factors influencing release of H_2S from liquid bitumen, therefore storage temperature should be maintained at a level not higher than operationally necessary.

[2] Council Directive of 12 June 1989 on the introduction of measures to encourage improvements in the safety and health of workers at work, (89 / 391 / EEC)

[3] https://www.cdc.gov/niosh/idlh/7783064.HTML

5.5. Protection of personnel

Personnel performing tasks where high levels of H_2S may be present should be made aware of the hazards associated with H_2S and properly trained to safely perform required tasks (e.g. loading, unloading). Appropriate personal protective equipment (PPE) should be used to address the identified hazards. An example of PPE may include wearing respiratory protection (e.g. a filtering face-piece respirator) when performing tasks or working in areas where it is expected that personnel may encounter higher levels of H_2S (e.g. confined spaces, non-routine operations).

5.6. Management of activities

Applying a "permit to work" programme may help eliminate or manage exposure to hazardous levels of H_2S (see Table 1).

- Confined space entry systems, including personal alarms
- Procedures for entering other areas where there is risk of high exposure to H_2S
- Escape routes equipped with windsocks that enable people to safely leave the area in the event of a release
- If possible work upwind of any potential H_2S sources
- Evacuation of non-essential personnel to a safe location if the concentration of hydrogen sulphide exceeds the occupational exposure limit (OEL). Note that OELs may vary by country or jurisdiction, see Appendix 1.
- Personnel should allow gases and vapours to dissipate before getting very close to tank openings. Avoid breathing the vapours very close to tank openings.

5.7. Exposure reduction

Exposure should be minimised by using technical means such as increase of automation of tasks with risk of exposure to high concentrations of hydrogen sulphide, for example introducing new techniques to enable opening of the man-lid remotely. Develop efficient procedures to minimise the time the worker is exposed to the hazard.

5.8. Training

Personnel should be educated about hydrogen sulphide including (training to raise awareness and provide competence, ensure effectiveness of training provided):

- Where such substances may be present
- How personnel can be exposed
- The potential effects on health following exposure
- How such substances can be detected
- The use and limitations of PPE (Personnel Protection Equipment)
- The use of gas monitors, including limitations, false readings and conditions of use)
- Alarms and Emergency procedures
- Ensure effectiveness of training

5.9. Access control

Entry and exit of people into the areas where hazardous levels of hydrogen sulphide might be present should be controlled, e.g. sign in/out system via permit officer in control room, electronic sign in/out system. In certain circumstances, a two-way radio communication system could be useful.

6. RESCUING EXPOSED PERSONNEL

In the event that a person is overcome and has lost, or is losing consciousness:

- Only personnel authorised and trained in rescue should approach the victim
- Contact facility personnel immediately to inform them of the emergency and to call an emergency medical service
- If possible, remotely stop any loading or transfer of operations
- Do not approach the victim without using supplied-air respirators (SAR) or self-contained breathing apparatus (SCBA). If you have the appropriate respiratory protective equipment, remove the victim from the contaminated area crosswind of the release. Rescue should be conducted with backup personnel also equipped with supplied-air respirators
- When in a safe area, arrange for first aid and initiate a medical response
- Keep the victim lying down
- If you are trained to do so, start cardiopulmonary resuscitation (CPR) if the victim heart has stopped beating
- If the victim's eyes are affected by H_2S, flush them thoroughly with clean, cool water
- Seek medical attention as soon as possible in every case of over-exposure. The effects of over-exposure to H_2S may be delayed and extended medical observation may be necessary
- Review established emergency medical procedures with local primary medical care and/or first responder staff

Examples of preventative activities that can be taken to reduce worker exposure to hydrogen sulphide are given below:

- First step is an assessment of the hazard on the site
- Ventilating the area to decrease risk
- Based on this assessment, signs should be provided that warn the loader and unloader that hydrogen sulphide may be present
- Personal or collective H_2S detectors should be made available to those performing the loading if other risk management measures are not already in place
- Appropriate control measures should be applied at delivery sites to reduce the residual quantity of hydrogen sulphide potentially present; this may include delineation of zones, information panels, driver training, documentation, use of adequate local ventilation
- Endeavour to stand upwind and avoid breathing the vapours, which escape when the manhole is opened, or closed. After unloading bitumen, personnel should allow gases and vapours to dissipate before closing the manhole
- It is recommended to automate, as far as possible, each potential hazardous task

7. CONCLUSIONS

On the basis of the information obtained from data submitted by its member companies, Eurobitume considers that there are some activities that may lead to potentially hazardous exposures to hydrogen sulphide during the loading and discharge process. Operations of loading/unloading, tank sampling and any activities close to manholes or ventilation pipes should therefore take the potential presence of H_2S into account. Consequently, all employees dealing with bitumen should be informed and trained to recognise potentially dangerous situations in relation to H_2S and employers should carry out a comprehensive risk assessment.

APPENDIX 1 – SELECTED ENTITIES ISSUING OCCUPATIONAL EXPOSURE LIMITS

Country	Authority
Austria	Grenzwerteverordnung 2011 - GKV 2011
Belgium	Belgisch Staatsblad 30 juni 2011; N. 2011-1687
Bulgaria	РБ МТСП и МЗ Наредба №13/2003
Czech Republic	178/2001 (12/2007)
Denmark	Arbejdstilsynet; Grænseværdier for stoffer og materialer, augustus 2007 (publicatie C.0.1)
Estonia	Sotsiaalminister 10/2007
Finland	Työterveyslaitos, Sosiaali- ja terveysministeriö 07/2009
France	Valeurs limites d'exposition professionnelle aux agents chimiques en France; INRS ED 984; juin 2008 (mandatory based on the decree May, 2012)
Germany	TRGS 900; version april 2011
Hungary	EüM-SxCsM 12/2007
Ireland	Health & Safety Authority
Italy	EU OEL/ list of indicateve OEL values 12/2009
Latvia	LV National Standardisation and Meteorological Centre 05/2007
Lithuania	Del Lietuvos Higienos Normos 10/2007
Luxembourg	EU OEL; List of Indicative OEL values 12/2009
Netherlands	Zoek een grenswaarde : In de Databank Grenswaarden Stoffen op de Werkplek kunt u opzoeken welke grenswaarde er is vastgesteld
Norway	Nye administrative normer for forurensning I arbeidsatmosfaere; utgave desember 2011
Poland	Ministra Pracy i Polityki Społecznej (Poland, 7/2009)
Portugal	Instituto Português da Qualidade
Slovakia	Nariadenie Vlady Slovenskej republiky
Spain	Límites de Exposición Profesional para Agentes Químicos en España, 2012; Ministerio de Trabajo e Inmigración, INSHT
Sweden	AFS 2005:17
Switzerland	SuvaPro Grenzwerte am Arbeitsplatz 2009
UK	Health & Safety Executive EH40/2005
OSHA[USA]	United States Department of Labor
ACGIH[Ad]	American Conference of Governmental Industrial Hygienists (United States)
NIOSH[AD]	National Institute for Occupational Safety and Health (United States)
SCOEL	Scientific Committee on Occupational Exposure Limits

[Ad] Advisory bodies
[USA] North American Value

APPENDIX 2 – HYDROGEN SULPHIDE BIBLIOGRAPHY

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