

**SULPHUR FIRES**

**- INFORMATION PACKAGE -**

*FOR FIREFIGHTERS &*

*EMERGENCY FIRST RESPONDERS*

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## **SAFETY AND FIRE FIGHTING TIPS**

- **Always use Self Contained Breathing Apparatus (SCBA). Sulphur fires produce hazardous sulphur dioxide gas.**
- **Sulphur dioxide gas is heavier than air and will accumulate in the vapour spaces of the rail car.**
- **Small sulphur fires are easily extinguished by adding more sulphur on top of the burning sulphur. This depletes the oxygen and smothers the fire.**
- **For larger sulphur fires use a light water fog or CO<sub>2</sub> to extinguish. Do not use heavy water streams as this may create sulphur dust which could potentially explode. Heavy applications of high pressure water may create environmental ground contamination as the high water pressure may drive the sulphur out of the rail car and on to the ground.**

## **DISCLAIMER**

The information provided in this document is for guidance only. It is based on what is believed to be sound data, experienced advice and best practice. The authors accept no responsibility or liability for its use by others in any circumstances

The flame propagation test demonstrated in the presentation utilizes Prill product. All other types of commercially formed sulphur, such as Rotoform, Slates, Pellets or Granules would produce the exact same results. That is, none of these forms of elemental sulphur are classified as a flammable solid.

## Introduction

This Information Package has been prepared for the guidance of those who must respond to the challenge of fighting fires involving elemental sulphur. More particularly the specific applications cited focus on fires in commercially formed solid elemental sulphur being transported in open rotary dump gondola rail cars.

The package consists of this document and an accompanying video illustrating various aspects of the ignition, combustion and extinguishing of sulphur fires.

While this document makes reference to much of the material covered in the video, it also contains additional material that is not included. This additional material provides extended coverage of topics commonly found in Material Safety Data Sheets and may be useful in training courses on the subject of sulphur and its burning characteristics and hazards.

## SULPHUR – An Overview

Elemental sulphur comes from two main sources. It is mined from deposits of the element in the earth, recovered from sulphur containing gases, such as hydrogen sulphide that are produced from natural deposits (usually in conjunction with gas or oil) or from industrial processes.

The sulphur is first produced in liquid form and it is either stored, handled and transported in that form or it is commercially formed into pastilles, pellets, granules, slates or other shapes by cooling and solidifying the liquid. The ease with which sulphur can be melted and resolidified is an important factor in understanding how it burns. It is the handling of fires in these solid commercial forms of elemental sulphur that is the main focus of this document.

The worldwide annual tonnage of elemental sulphur used is one of the highest of all chemical raw materials. Tens of millions of tonnes find their way into a wide variety of products – namely fertilizers, chemicals and various acid industries. Typically it is first converted into sulphuric acid which is one of the key process chemicals in industry. The first step in this process, is the **burning** of sulphur to form sulphur dioxide, exactly what happens in a burning sulphur rail car. The predominant use of sulphur in the fertilizer industry is through the manufacture of sulphuric acid which is then used to extract the phosphorous (P) for fertilizer from ore rocks. Transporting elemental sulphur for acid and phosphate fertilizer manufacture is a key component to feeding the world's growing population and it is much safer to transport compared to the acid it is used to produce.

Canadian recovered sulphur is typically shipped at greater than 99.9% purity. It is this exceptional purity which gives Canadian producers a significant advantage in selling their product to end users all over the world for multiple applications.

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**PRODUCT IDENTIFICATION AND TDG REGULATIONS****COMMERCIALY FORMED ELEMENTAL SULPHUR**

<b>UN (United Nations) PIN</b>	1350 – SULFUR; or SULPHUR
<b>CAS# (American Chemical Society/Abstracts)</b>	7704-34-9 (all elemental sulphur)
<b>IMSBC (International Maritime Solid Bulk Cargoes Code- adopted in 2008)</b>	Sulphur (formed, solid) Group C (Non-hazardous cargo)

Solid elemental sulphur is listed in Transport of Dangerous Goods regulations as a Class 4.1 Flammable Solid, Category I.. with special provision 33 which **EXEMPTS** commercially formed sulphur from classification under Transport of Dangerous Goods Regulations as a Class 4.1 flammable solid.

This exemption resulted from the test data submitted to the regulatory authorities on the rate of flame propagation in standard tests of the various types of commercially formed solid elemental sulphur that are commonly used in rail shipment of the product. The details of the tests are presented in the video part of this package and the results were accepted by the UN sub-committee on Transportation of Dangerous Goods leading to the exemption ruling.

As result the Schedule 2 special provision 33(b) was applied to UN1350 Sulphur – which states “these regulations do not apply to these dangerous goods if the dangerous goods have been formed to a specific shape such as prills, granules, pellets, pastilles or flakes”.

Notwithstanding the exemption, it is common to find the UN 1350 signage on rail cars dedicated to the haulage of solid elemental sulphur.

## PHYSICAL STATE

**SOLID:** Commercially Formed into Granules, Pellets, Prills or Pastilles of generally spherical or hemispherical type; or into more two dimensional Flake or Slate types.

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The physical state description above applies to Canadian Bright Yellow Elemental Sulphur, in bulk, as shipped by rail to West Coast Terminals for export to overseas customers. It is important to recognize this particular physical state in connection with product classification under transport, storage and handling regulations. The combustion propagation characteristics of these forms may be considerably different from other physical forms of sulphur having the same chemical purity. Other forms are described as being in the following physical states - Lump, Crushed Bulk, Flowers of Sulphur, Sulphur Flour Micronized Sulphur, Stick, Powder, Crude, Screened Crude sulphur among others.

## **APPEARANCE, ODOUR AND HAZARDOUS INGREDIENTS**

Commercially formed solid elemental sulphur is generally bright yellow in colour. If the solid sulphur is off-yellow it is usually due to impurities. This should not be confused, however, with the colour of liquid sulphur which is formed when the solid melts as it does from heat of combustion. The colour of liquid sulphur is the best indicator that the sulphur is very likely burning.

Yellow sulphur first melts to a golden coloured free-flowing liquid. As its temperature rises, the colour turns to orange, then dark red and finally black. All of these colours may be seen in a pool of burning liquid sulphur as is clearly seen in several of the shots in the video presentation.

Pure elemental sulphur is essentially odourless and is considered to have a very low toxicity towards humans. Any smell attributable to solid sulphur can usually be associated with impurities. The most common one is hydrogen sulphide – similar to the smell of rotten eggs. In recent years the practice of “degassing” the liquid sulphur before it is solidified into the various commercial forms has greatly lessened this reaction. Please note comments under Exposure Limits (Pg.22) regarding exposure to hydrogen sulphide.

Human senses reaction to solid elemental sulphur is usually the result of contact with and/or ingestion of small amount of fine particulate sulphur dust. It has a slightly acidic taste and can result in uncomfortable irritation if it gets into the eyes, which is agitated further by rubbing. The most common route of dust entry to the eye is through hair and eye lashes eventually entering the tear liquid. ***It is strongly recommended that enclosed eye protection be used in and around elemental sulphur.***

The low level of human toxicity is well illustrated by the common use of “sulphur and molasses” as a Spring Tonic before the advent of more sophisticated medications. The LD 50 for elemental sulphur is greater than a 12g dosage given orally. This would be the equivalent of swallowing nearly 500 of the pastilles of one of the commercially formed products. ***Fine sulphur particulate dust is more likely to have undesirable effects on the human airway system and wearing appropriate filter masks is recommended.***



## **Burning Properties of Sulphur**

### **- Summary -**

- Combustible solid
- Not easily ignited
- Slow burning, pale flame
- Melts to dark, red-brown liquid
- Combustion product is toxic
- Sulphur dioxide is heavier than air
- Avoid unnecessary disturbance
- Sulphur dust can be explosive (in high concentrations)

## **KEY BURNING PROPERTIES OF SULPHUR - OVERVIEW**

***The most significant difference between elemental sulphur and many other solids that burn is that sulphur must first melt before it burns.*** This means that the ignition source must have enough thermal energy in it to heat a small portion of elemental sulphur to at least 120°C before ignition by a hot source occurs.

The **melting point (119 °C)** of sulphur is just above the boiling point of water. Once it melts, the vapour pressure of sulphur above the liquid surface is high enough to sustain combustion in the vapour phase above the liquid. Critical to the continued burning of sulphur, however, is the continued supply of an air stream across the burning surface. This does two things - it supplies oxygen needed for the sulphur to burn and sweeps away the sulphur dioxide combustion product which is heavier than air. If the sulphur dioxide is not swept away from the seat of the fire it settles there and acts as a fire extinguisher like carbon dioxide.

This is why so many of the small fires that may be ignited by hot coke cinders from locomotive exhausts are not sustained, especially if the train is not moving and generating air flow over the sulphur surface. ***It is also the reason why care should be exercised when entering a sulphur laden rail car.*** It is almost certain to be stationary when this is done and, if the fire is extensive enough, the sulphur dioxide combustion product may rise away from the seat of the fire (thermal lift) but settle back into the air space of the car, below the gunwales. The concentration of sulphur dioxide in that airspace may thus be well above the toxic level.

***It is for these reasons that rail cars suspected to have a sulphur fire should be approached from upwind.*** If inspection over the gunwale shows the presence of a dark brown/red stain or pool of liquid sulphur, usually along the side of the car, this strongly suggests that the sulphur is burning, as seen in the video. This means that the rail car head space is likely filled with sulphur dioxide gas at a dangerous level. ***The car should not be entered without use of breathing apparatus.***

## Key Temperatures, Weights and Measurements

	Celsius	Fahrenheit
Melting Point	<b>112-119°C</b>	<b>234-248°F</b>
Boiling Point	<b>444°C</b>	<b>831°F</b>
Flash Point (for liquid melt)	<b>168°C</b>	<b>335°F</b>
Auto-Ignition Temperature		
Liquid Surface	<b>248-261°C</b>	<b>478-502°F</b>
Dust Cloud	<b>190°C</b>	<b>375°F</b>
Lower Explosive Limit (dust/fines)	<b>35g/m<sup>3</sup></b>	
Upper Explosive Limit	<b>1400g/m<sup>3</sup></b>	
Minimum Ignition Energy	<b>15 mJ (low)</b>	
(Electrostatic sparks can ignite dust)		

## **Key Temperatures, Weights and Measurements**

The **Boiling Point** of sulphur (**444°C**) is unlikely to be reached simply as a result of liquid sulphur burning in air. However, in the presence of oxidizing agents or other hot burning materials, such as might be the case with other commodities being hauled in bulk in adjacent cars on adjacent track, temperatures in excess of 444°C are possible. Under these conditions high concentrations of readily combustible sulphur vapour are possible in and around the location of the fire. Such hot sulphur vapour combined with high concentrations of sulphur dioxide combustion product could represent a lethal mixture for unprotected personnel close to the fire.

The lowest value reported for the **Flash Point** of sulphur (**168°C** - Cleveland Cup Method) is substantially above the melting point. Thus solid elemental sulphur does not really have a flash point since it must be liquid before the flash point temperature is reached. Note that these remarks apply to sulphur in bulk and not finely divided particulate dispersed in air (dust - see LEL and UEL, Pg. 12). It is also interesting to note that the flash point is just above the temperature at which liquid elemental sulphur begins to turn into a dark, viscous fluid (equilibrium polymerization temperature 160°C). If the liquid is still golden yellow it is not likely to flash.

The **Auto-ignition Temperature** (**248-261°C**) again applies to the **liquid phase** only since solid sulphur melts well below this temperature. It is unlikely that sulphur would exist at this temperature and not already be burning, but it is possible if there is an external heat source such as burning fuel on the outside of the rail car. If this were to happen then the liquid sulphur would auto-ignite in air without a need for a specific ignition source.

Of greater significance is the much lower **Auto-ignition Temperature of a dust cloud of sulphur** (**190°C**). Such dust clouds may be generated if bulk solid sulphur is disturbed, say by high pressure fire fighting equipment. Hence the strong preference for not using such methods for extinguishing sulphur fires. If the particulate size in the dust cloud is small enough, the ignition can lead to very fast combustion i.e., explosion. This was one of the reasons behind adoption of commercially formed solid elemental sulphur as the preferred form for transportation. The Premium types of such forms are noted for their low dust content and low friability during handling. Nevertheless, **DO NOT DISTURB** is a key to fighting sulphur fires.

**Lower (LEL) Explosion Limits** for sulphur dust or fines is **35g per cubic meter**. The important value as far as fire fighting is concerned is the LEL. At 35g/cubic meter, fine sulphur particulate is among the more readily detonated powders commonly found in bulk commodity handling. This emphasizes the need to avoid creating a cloud of sulphur dust especially with flame or hot surfaces in the vicinity. Crawler tractors passing over or through dry spilled sulphur are particularly susceptible to agitating sulphur dust which can “pop” and/or ignite on contact with hot exhaust manifolds.

**The Minimum Ignition Energy of 15mJ** for sulphur dust clouds above the LEL is also a low value compared with many other explosive dusts. This means that electrostatic sparks generated by frictional interaction of sulphur with an insulating material - such as most plastics, can create spark discharges of sufficient energy to ignite LEL concentration dust clouds. The potential for detonation of sulphur during fire fighting should be kept in mind at all times.

**Incompatibility with Other Substances** is primarily related to oxidizing materials. Sulphur should not be stored or transported in close proximity to strong oxidizing agents such as fluorine, chlorine, chlorates, nitrates, nitric acid, peroxides, liquid oxygen, permanganates, dichromates and the like. Sulphur powder may ignite spontaneously when mixed with powdered coke if the appropriate catalytic conditions are present. It also can react with sulphuric acid to form polythionic species, thus appearing to dissolve in the acid.

Thus it is important to determine the nature and proximity of other materials in any mixed consist set of rail cars in the event of fire in order to assure that no incompatible material is in close proximity to any sulphur cargo. It is of **prime importance** to keep in mind that the **greatest hazard in a sulphur fire is the sulphur dioxide combustion product** and this is commonly generated whenever sulphur is oxidized by fire or chemicals.

## **AFTER THE FACT EVIDENCE OF A SULPHUR RAIL CAR FIRE**

From time to time firefighters and others may be called upon to inspect sulphur carrying rail cars that may have been reported to have been “on fire” but no fire is visible upon later inspection. What is the evidence that a fire may have been present in the cargo at an earlier time?

The photographs in this section attempt to answer that question and to provide some additional information on how the burning process actually occurs in the sulphur.

Photo 1 (Pg. 16) shows the aftermath of a small fire in a sulphur rail car. Note that there is no readily observable discolouration of the sulphur such as is seen in the video of actual burning commercially formed sulphur in test vessels. The dark red/brown colour that is observed in the video is a characteristic of the hot, burning liquid sulphur and when the fire goes out, and the sulphur cools and solidifies, it returns to its bright yellow colour.

Note in Photo 1 (Pg. 17) however, that particulate formed sulphur has agglomerated into cakes of sulphur on the surface of the cargo. Close inspection of this cake as seen in Photos 3 and 4 (Pg. 18) show that the particles of the formed sulphur have fused together (melted) and this is a sure sign that there has been a fire at or near that spot on the surface.

Photo 2 (Pg. 17) shows where the fire probably started. Note that most of the caked sulphur is along the inside sidewall of the rail car, but there is clearly a part of the effected surface area that “swells out” into the middle of the car. It is at the peak of this “swell” that the fire very likely was ignited. Some hot ignition source fell at this spot, melted a small pool of sulphur as is demonstrated in the video and then, with the aid of some airflow, ignited the liquid. As this fire expanded the liquid sulphur ran down from the peak stow of the sulphur where it had begun, and collected along the trough between the peak stowed cargo and the side of the rail car. This mechanism is also demonstrated in the video.

If a thorough inspection of a suspected rail car fire is to be made, it is advisable to first look over the gunwales of the rail car to establish the location and the pattern of the fire evidence before actually entering the car and possibly destroying the evidence with footprints.

The close up inspection of the cake resulting from the fire is seen in Photos 3 and 4 (Pg. 18). Note that the top (burning) surface has been completely liquefied and there is little or no evidence remaining of the particles of the commercially formed sulphur. Indeed the folded nature of the resolidified surface suggests that the rail car was probably moving when that part of the surface resolidified and the ripples on the surface of the liquid were frozen in place.

As we move down through the cake toward the underside it is clearly seen that the liquid sulphur generated by heat from burning at the surface permeated down through the particles, melting some and cementing others that were deeper into a solid mass. The fire liquefies the sulphur at the surface but liquid below the surface cannot burn without oxygen. The liquid drains down into the cold particulate sulphur below and then freezes solid to form a mass of caked particulate.

The level of maximum penetration down into the cargo is marked by a thin black line clearly seen in the photographs. It is suspected, but not proven, that this black material is the residue of the ignition source (carbon) and it is a nice straight line because it marks a liquid drainage level in the sulphur.

Below the black demarcation line we begin to see particles of the commercially formed sulphur again. These are stuck to the lower surface of cake embedded in the lowest level that the liquid sulphur drained down to before it solidified. Below this level the particles of sulphur are free flowing and unaffected by the heating events that occurred above them.

It is important to note the relatively shallow depth of penetration of either the heat or of the liquid sulphur. This is certainly due to the fact that sulphur is an excellent thermal insulator. A few inches of sulphur is more than enough to sustain thermal insulation between regions at 200°C and 20°C. Ample evidence of this thermal insulating property is seen in various shots in the accompanying video presentation.

An important practical consequence of this shallow penetration is the question of whether it is necessary to dig down into the sulphur cargo to insure that the fire is out - as for example in forest fires. Every observation from sulphur fires in rail cars supports the view that the fire does not penetrate much below the surface. This is explained by the fact that sulphur cannot burn without oxygen. As the liquid sulphur drains into the mass of particulate below it drives out the air between the particles and that zone, though still hot, is anaerobic. Therefore there is no combustion. If there is enough air to support combustion below the surface before liquid sulphur drains into it, the sulphur dioxide combustion product that forms is heavier than air and tends not to rise to allow more air to reach the seat of combustion. The fire below is self extinguishing.

***For these reasons and others, it is demonstrated that disturbing a burning sulphur surface is not a good idea.***

It is useful to examine the site of the suspected fire for evidence of residues of the original ignition source. As demonstrated in the video and has been elaborated here these sources need only be a few millimeters in size and may well burn away to leave only fine black ash which sinks into the liquid that drains down into the cargo (black line in Photos 3 and 4 Pg. 18) . If there is evidence of residue, its location relative to the evidence of the fire should be recorded, and if possible samples recovered.



## PHOTOS OF AN ACTUAL RAIL CAR SULPHUR FIRE



*Photo #1 Aftermath of a small fire*



*Photo #2 Point of Fire Ignition*

**PHOTOS OF AN ACTUAL RAIL CAR SULPHUR FIRE**



*Photo #3 Caking of sulphur on surface of cargo*



*Photo #4 Fusing of melted sulphur. NOTE: Particles underneath remain intact.*

## **FIGHTING SULPHUR FIRES**

In this section we have attempted to collect together in short paragraph form some of the essential do's and don'ts of fighting a sulphur fire, with special reference to fires in commercially formed solid elemental sulphur being transported in open gondola rail cars. The list is not necessarily exhaustive, but it does attempt to focus on some of the more salient features of the challenge.

1. The flame from burning sulphur may not be very visible in bright sunlight. What is obvious is the red/brown colour of the hot liquid sulphur on the surface that is always associated with burning sulphur.
2. The combustion product is toxic sulphur dioxide gas. It is heavier than air and may not disperse from the scene of the fire very readily. It may be trapped in the "headspace" above the sulphur and below the gunwales of the gondola car. Do not enter the car unless wearing breathing apparatus.
3. Approach the fire from upwind.
4. If the fire is not extensive, it may be possible to extinguish it by smothering it with more sulphur that is at hand and not burning. This is a quick and effective method of extinguishing small sulphur fires.
5. The burning sulphur surface should not be disturbed by use of high pressure jets of water or other extinguishing medium. Use fine sprays of water or snuffing steam or extinguishing foams such as carbon dioxide. Use of halogen based fire extinguishers is not recommended.
6. It is very unusual for a sulphur fire to penetrate deep into the underlying sulphur cargo. Drainage of liquid sulphur into the lower levels of the cargo excludes air essential for combustion and the combustion product itself. Sulphur dioxide, tends to remain around the seat of the fire also preventing ingress of air needed for further burning. It is thus not necessary to dig deep into the cargo to insure that the fire is out. Removal of the surface cake of fused sulphur is usually enough to ensure that there is no slow combustion at deeper levels.
7. In the event that other materials (fuel, oils, chemicals etc.) are burning in the immediate vicinity and generating high temperatures, be cautious about the autogenous ignition of sulphur if it is heated by such adjacent high temperature sources.
8. Sulphur is not compatible with oxidizing chemicals and may combust explosively in their presence.

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**KEY WARNING - BEWARE SULPHUR DIOXIDE - THE MAIN HAZARD****HUMAN IMPACT, FIRST AID, PROTECTIVE CLOTHING**

In this section we provide an overview of some the safety/health issues which should be considered by responders to sulphur fires – either small or large.

Humans have very little immediate reaction to contact with solid elemental sulphur in bulk form. The most obvious reactions are to the fine particulate dust form of solid elemental sulphur, not to the particulate sizes that are common in commercially formed solid elemental sulphur.

Recent reports of negative results from acute exposures to high concentrations of fine particulate sulphur dust are relatively few due in large part to improved industrial hygiene.

Attending a sulphur fire, however, introduces the possibility of exposure to uncommon conditions with respect to sulphur, not only in its solid form but in its liquid form and to by-products of combustion.

What follows are some observations and advisory comments that may assist in insuring the safety of fire fighting personnel.

## SENSITIZATION / DESENTIZATION

<b>Sulphur:</b>	Susceptible individuals may have increased sensitivity to exposure.
<b>Sulphur Dioxide:</b>	All individuals sensitive to sulphur dioxide.

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Elemental sulphur dust is not a sensitizer/desensitizer, as defined under WHMIS. Persons with particularly sensitive skin or mucous systems (eye and respiratory) should exercise caution with respect to repeated or prolonged exposure to elemental sulphur. While the substance has been used in salves and ointments to treat skin disorders, reaction between finely divided particulate sulphur and normal skin fluids may yield products to which certain skin tissue is sensitive. Certain individuals also react more rapidly and extensively to the ingress of sulphur particulate into eye and airway passages. New staff reaction to prolonged exposure should be monitored.

Sulphur dioxide, the product of combustion of elemental sulphur is a highly toxic suffocating gas, that irritates human and animal airways due in part to its acidity. All individuals react and are sensitive to low concentrations of sulphur dioxide, Initial reaction is usually coughing followed by extreme shortness of breath and rapid collapse if the individual is not removed from the effected area and into fresh air. Sensitivity of humans to sulphur dioxide is significantly greater than sensitivity to sulphur or even sulphur dust.

## IRRITANCY

<b>Commercially Formed Elemental Sulphur</b>	Very mild on skin contact
<b>Associated dust/fines:</b>	Eye - moderate; Airway - slight
<b>Associated Products:</b>	
<b>Hydrogen Sulphide:</b>	Severe local irritant
<b>Sulphur Dioxide:</b>	Severe local irritant

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While solid elemental sulphur does not meet the WHMIS criteria for classification as an irritant, irritation to the human system arising from solid sulphur can result from fine particulate contact with the eye. Even walking through an area in which solid sulphur is being handled can result in fine particulate depositing on or near the eye, especially on the hairs of eyebrows or other head hairs. When such a particle of solid sulphur eventually enters the eye (there is often a time delay of minutes to an hour) the irritation by the foreign body of the sensitive eye tissue and fluid is usually experienced. This often leads to involuntary rubbing of the eye which, almost inevitably, makes the situation worse by forcing more particulate into the eye socket area. These fine particulates may then undergo slow chemical reaction with the eye fluids to produce acidic conditions which can lead to profuse tear formation - natural defense mechanism.

Reaction with skin is less common but can occur on unprotected skin particularly if covered with perspiration. Dust/fines can cause mechanical irritation of the nose and throat. Sulphur dust did not cause significant upper airway sensory irritation in mice; at the maximum achievable air concentration of 451 mg/m<sup>3</sup>.

While the associated products are classified as severe irritants their other toxicological effects will likely be more pronounced at any given concentration. In the case of sulphur dioxide it should be noted that this gas dissolves readily in water (body surface fluids) to form moderately strong protonic acid solutions with the normal acidic irritancy associated with these substances.

## EXPOSURE LIMITS

<b>Formed Elemental Solid Sulphur:</b>	None		
<b>Sulphur Particulate Dust:</b>	8hr OEL	10 mg/m <sup>3</sup>	(Alta. OHSR)
<b>Total Hydrogen Sulphide Ingredient:</b>	8 hr OEL	10 ppm	(Alta. OHSR)
	Ceiling Value OEL (Alberta)	15 ppm	(Alta. OHSR)
	STEL / Ceiling Value (British Columbia)	10 ppm	(BC: OHSR)
<b>Hydrogen Trisulphide &amp; other volatile polysulphides (H<sub>2</sub>S<sub>x</sub>):</b>	As per Hydrogen Sulphide (refs 22 & 27)		
<b>Sulphur Dioxide Combustion</b>	8 hr. OEL / TWA	2 ppm	(Alta & BC. OHSR)
<b>Product:</b>	Ceiling Value OEL / STEL	5 ppm	(Alta & BC. OHSR)

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The data in the table above clearly indicates that it is not the toxicity of the Commercially Formed Solid Elemental Sulphur that imposes significant exposure limits but rather that of the trace amounts of sulphur by-products that may be evolved or that of toxic combustion products. Nonetheless, consideration should be given to the extent to which there may be a duty to provide the appropriate data that warns of these secondary hazards in the MSDS for Commercially Formed Elemental Sulphur.

It has been noted elsewhere in this document that evolution of hydrogen sulphide has become less of a potential hazard since the more general adoption of degassing technologies that reduce residual hydrogen sulphide in recovered sulphur to very low levels. The potential for release of hydrogen sulphide into head space of liquid sulphur rail tank cars may still exist, however, and care should be exercised in dealing with fires involving such cargoes. It should be noted also that any such hydrogen sulphide will burn to sulphur dioxide should it be released with burning sulphur.

The exposure limits shown above clearly establish that sulphur dioxide, which will always be present around a sulphur fire, actually has a lower exposure limit than hydrogen sulphide. Although its physiological mode of action on humans is different from that of hydrogen sulphide, it is nonetheless a potent toxic gas and must be treated as such. Its presence at sizable concentration levels is assured at every sulphur fire.

## ROUTE OF ENTRY

### Solid Sulphur Component:

<b>Skin Contact:</b>	Minimal over short time periods; protective cover recommended.
<b>Skin Absorption:</b>	Fine particulate may lodge in skin crevices and be slowly assimilated; thorough cleansing recommended.
<b>Eye Contact:</b>	Undesirable; causes irritation and possible acidic damage; use of eye protection goggles highly recommended.
<b>Inhalation:</b>	TWA (Time Weighted Average) total dust = 10 mg/m <sup>3</sup> : Alberta OHSR - Chem. Haz. Reg. 393/88. Approved respiratory protective device recommended in dusty conditions.
<b>Ingestion:</b>	No recent test data; Lethal Dose > 12g (human) (See U.S. Dispensatory).

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Commercially Formed Solid Elemental Sulphur has limited potential for entering the human system. The relatively large size of the particulate forms requires a conscious action for ingestion and they are unlikely to invade the system by other routes of entry. However, the small amount of fines or dust generated during handling can present a potential for entry by inhalation. Major consequence of contact with the eye is likely first that of mechanical irritation of fine particulate lodged in the eye but subsequently may be due to acidification. Effect usually enhanced by normal reaction of rubbing irritated eye.

Effective entry of hydrogen sulphide into the human system is almost exclusively by inhalation. Because of the very high toxicity of hydrogen sulphide, exposure should not be permitted on any basis in excess of permitted limits.



## **FIRST AID PROCEDURES**

The selection of specific measures that should be included in the MSDS section on First Aid should be carried out by the individual preparing the MSDS, with advice from colleagues who are best familiar with the kinds of emergency situations that are likely to arise during the handling, storage, transportation and end use of the product. The material that is presented here is a compilation of First Aid Procedures that have been published in a variety of MSDS's on sulphur and which have been encountered through experience. It must be EMPHASIZED that these first aid procedures refer to Commercially Formed Solid Elemental Sulphur and represent FIRST AID not professional medical attention. In every case where emergency treatment of the kind referred to here is applied, the responsible individuals at the scene and in particular the persons effected must be the judge as to whether immediate follow-up professional medical attention is indicated. As is common practice the information detailed below is categorized by the body part effected by contact with the product.

### ***SOLID ELEMENTAL SULPHUR***

#### **Eyes**

The eyes are the most sensitive part of the individual that most often require first aid in the event of exposure to airborne solid sulphur fines (see Toxicological - Routes of Entry Pg. 24). By far the most frequent reaction is that of irritation with no lasting effects provided appropriate protection measures are taken – ie. protective eye wear. Longer term exposure can have greater effects. First aid treatment may consist of persistent (15 min) flushing of the eye and its surroundings with cool fresh water. Eyelids should be held apart to ensure that all eye surfaces are gently flushed. Repeated use of “eye bath” in First Aid kits may be effective but it is more the volume of flushing that appears to be effective. Care should be taken to ensure that sulphur particulate is thoroughly removed from surrounding hair covered areas - especially eyelashes. Prolonged exposure to standard shower spray is often effective. Post-event monitoring for eye irritation is recommended and professional medical attention should be sought in the case of positive indications.

### **Inhalation**

Affected persons should be removed from dusty area to fresh dust free area as soon as possible. Caution should also be exercised in determining whether effects are due to sulphur dust inhalation or inhalation of other ingredients such as hydrogen sulphide (see below). Short term effects of inhalation of minor amounts of sulphur dust are not likely to be major but post event monitoring is advisable.

### **Ingestion**

Solid sulphur ingested in small doses is not toxic (traditional “sulphur and molasses”). More massive doses may require first aid followed by medical attention. Ingestion of large volumes of cool fresh water have been suggested in some MSDS’s.

### **Skin**

Normal healthy skin does not react quickly when contacted by solid elemental sulphur. Extensive skin exposure to solid sulphur particulate may require thorough washing of the skin with mild soap and water. The solubilizing effect of the soap on the sulphur particulate (micelle formation) helps water remove the particles. Dust laden clothing should be thoroughly cleaned before being worn again. In the event of irritation or if rashes develop, professional medical attention should be sought.

## ***LIQUID ELEMENTAL SULPHUR***

### **Burns**

Liquid elemental sulphur produced by melting during sulphur fires has a particular propensity to cause serious burns if it reaches human skin. The liquid, always above 120°C, can not only scald like boiling water, but is likely to remain at the site of contact because it will solidify on contacting skin. Hot sulphur adhering to the skin will continue to transfer heat from its solid form to the skin at temperatures well in excess of 90°C and prevent the access of cooling air to the site.

For these reasons it is critically important that any person approaching a liquid sulphur source should be completely covered with some sort of protective clothing that will protect skin from liquid sulphur splashes. Equally important is the avoidance of any clothing, or manner of wearing clothing, that will allow liquid sulphur to gather in a crevice or fold next to the skin. As examples all pant legs should be worn **outside boots**, gloves should be worn with **cuffs inside sleeves** and collars should be **buttoned closed** to prevent liquid sulphur from lodging between skin and clothing.

## PERSONAL PROTECTIVE EQUIPMENT

Because of the descriptive nature of the information likely to be supplied under this section of the MSDS, no abbreviated form of entry is suggested for consideration. The material that follows is compiled from inspection of a variety of publications and other MSDS's and from experience in the field.

### **GLOVES**

Skin protection in general is recommended especially for workers who will be regularly and continually exposed to possible contact with solid sulphur dust. If actual handling of tools, samples etc. that may bring the hands into direct contact with sulphur is anticipated, the most important feature of glove wear is that it be impervious to the passage of the sulphur dust. It is equally important, however, to avoid glove wear that may prevent escape of perspiration. If hands become wet with perspiration this may encourage prolonged residence of sulphur dust in colloidal or suspension form net to the skin. Sulphur may also react with perspiration to form soluble sulphur compounds. The glove form should therefore be a compromise between preventing ingress of sulphur and permitting egress of perspiration vapors. Loose fitting gloves with large cuffs may be suitable. The gloves should also have at least modest chemical resistance to provide short term protection against acidity.

### **CLOTHING**

As in the case of gloves the most important property of clothing is to minimize, if not prevent, contact between solid sulphur particulate and skin, especially on a long term basis. Visiting or working in an area in which solid sulphur is being stored and handled by **any** individuals with extensive exposed body parts should not be permitted. Adequate coverage to prevent dust settling on the skin or hair while still allowing reasonable ventilation is very important. Loose, dust impermeable, full coverage is the preferred form of clothing. The clothing, like gloves, should have at least short term chemical resistance.

Fine sulphur dust has a substantial propensity to adhere to coarser fibre clothing materials such as wool. It is difficult to remove even by vigorous shaking. Clothing that is exposed to sulphur

dust should therefore be removed before leaving the operating site in order to prevent involuntary carriage of adhering sulphur dust into “clean” environments. Some automobile upholstery is equally susceptible to this type of contamination.

Human hair is another example of the kind of fibre adhesion mentioned above. Thus the exposure of hair should be minimized by wearing suitable headgear. A hard hat is often sufficient but a tighter fitting cloth cap under the hard hat is sometimes indicated. Exposed long hair, beards and mustaches can present special challenges.

Long sleeve shirts, outer jackets with no “open pockets” and trousers without cuffs are preferable in order to minimize spaces where particulate sulphur could accumulate over time.

### **FOOTWEAR**

The primary requirement of footwear is that it be of such a design as to prevent entry of formed sulphur particulate. This is especially important for individuals who may be required to walk on the surface of Commercially Formed Solid Elemental Sulphur in Bulk. While the practice is not recommended (see Physical Properties Pg. 7) it is sometimes unavoidable. Thus the connection between leg cover and footwear should be such as to prevent ingress of sulphur particulate. Normal industrial safety footwear with this added feature is normally adequate for regular use by workers.

In the event of a solid sulphur fire it should be remembered that solid sulphur usually melts as it burns due to the heat of combustion. Therefore, there is potential for brief but significant contact between footwear and small pools of burning liquid sulphur. The material of construction of the footwear should therefore be such as to withstand at least brief exposure to these conditions.

### **EYES**

Since eyes have been identified as probably the most sensitive part of the human system to the environmental contaminants around solid sulphur operations, their protection is of primary importance. It is strongly recommended that all personnel, visitors and workers alike, not be permitted to approach solid sulphur handling operations without wearing chemical safety goggles or their equivalent. Regular safety glasses are not considered adequate since they do not

provide lateral protection against ingress of sulphur fines which can become lodged on eyebrow hair etc. It is emphasized that it is not the IMMEDIATE reaction of the eye to the environment that is the main problem. This is part of the reason for the sometimes lax attitude toward such exposure. It is often very much a delayed reaction resulting from the eventual contact between the eye and sulphur “filtered out” on the eyebrows and the even more delayed acidification reaction that may occur between sulphur and the eye fluids.

### **RESPIRATORY PROTECTIVE EQUIPMENT**

There are two quite different requirements in this category. The first relates to protection against prolonged exposure to low levels of fine sulphur particulate. This is only likely to occur in the case of operators who, as part of their regular duties, are required to be at or close to areas where significant levels of inhalable dust (above  $10 \text{ mg/m}^3$  - see Exposure Limits (Pg. #23) may be occur. In such cases the wearing of a NIOSH approved particulate respirator mask is recommended.

The second, much more rigorous requirement, is for protection against inhalation of sulphur dioxide fumes generated as a result of combustion of solid sulphur in a fire. While such protection is obviously not required under normal conditions it must be immediately available in the event of fire. No attempt at firefighting of anything other than the smallest ignitions should be attempted by personnel who are not equipped with self-contained breathing apparatus.

The likelihood of toxic levels of hydrogen sulphide being encountered during the handling of SOLID elemental sulphur is small. As has been discussed in the section on Hazardous Ingredients, there are only limited circumstances when evolved hydrogen sulphide may accumulate to a level where self contained breathing apparatus is required by operators. Personnel, however, should be made aware of this application of available equipment.

### **INGESTION**

While ingestion is only indirectly a matter related to inhalation, it is worth noting here that consumption of food in the immediate vicinity of solid sulphur handling facilities should not be permitted.

## **BURNING SULPHUR - KEY POINTS**

- Not easy to ignite
- Melts to brown liquid – this is what burns
- Very viscous when hot
- Needs air flow to sustain
- Beware of toxic gas produced
- Easy to extinguish
- Do not disturb the surface
- Extinguish with more solid sulphur or use fine water spray / CO<sub>2</sub>