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Fire in hot asphalt cargo hold, spontaneous ignition during unloading

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1 Summary

While unloading hot asphalt from a marine tanker a fire broke out in the cargo hold. The likely cause was ingress of air caused by the unloading operation and subsequent ignition of asphalt deposits in the headspace due to the presence of pyrophoric iron sulphide compounds. While personnel were contemplating options and roles the fire suddenly intensified but it responded well to a foam attack when the decision eventually was taken.
2 The incident

The incident took place Monday morning 18 July 1977 at Gulfhavn, the oil terminal of Gulf Oil Refining near Skælskør, Denmark. Loading of the asphalt tanker M/T Engelsberg (Stockholm) completed at 07:55. Shortly after, the tanker crew noticed that the vessel had excessive draft indicative of overloading. An operator was dispatched to the asphalt tank TK90 and discovered that the tank level was approximately one meter lower than planned.

After some debating it was decided that the tanker should unload some of the cargo back into TK90. Unloading commenced at 09:05 but was halted at 09:15 when smoke was detected coming out of the hatches of the fore compartments.

The captain requested the assistance of two fire fighters through an offsite operator who relayed this information to the shipping agent. The message was passed on to the offsite control room and reached the refinery fire station 09:20 over the internal telephone system. The reason why two fire fighters were requested had been lost in transmission. Consequently, a fire fighter was dispatched to investigate. He returned to the fire station at 09:30. At the same time the offsite control room called the fire station again, now reporting fire. The fire alarm was sounded 09:32.

Upon arriving, the refinery fire crew contacted the captain. They decided that the vessel’s own high-expansion foam system would deal with the situation. The captain was not interested in the refinery’s medium-expansion foam. The tanker’s own foam system should be able to deliver ample amounts of high-expansion foam in 10-15 minutes time, but before this system became fully operational the generation of smoke suddenly intensified greatly. The captain then requested refinery foam.

Meanwhile three refinery foam eductors had been readied. Over the next 30 minutes 1,100 litres of refinery foam concentrate and 750 litres of the ship’s foam concentrate were applied. The fire was extinguished at 10:00 and the all-clear signal was sounded at 10:30. The original fire report (Gulf Oil 1977) holds no mention of causes.

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1 The refinery closed in 1997. The site continues as a tank terminal.
2 M/T Engelsberg was a 5,030 DWT asphalt tanker with a length of 123.1 m (Fakta 2011)
3 The diameter of tank TK90 was about 23.0-23.5 metres, a level difference of about one metre would correspond to about 420 m³.
3 Pyrophoric iron sulphides

Davie et al. (1993) studied iron sulphide as a possible ignition source in the storage of heated bitumen. They argued that pyrophoric iron sulphides form in oxygen deficient atmospheres. The suggestion is that rust from the tank will react with any available hydrogen sulphide. Hydrogen sulphide and other sulphur-containing compounds have been found in the vapour space of bitumen tanks. The hydrogen sulphide may build up in confined spaces such as a tank head space to reach high concentrations. Rust can form within the storage space on exposed surfaces such as manway covers and inside vents or may be present on the underside of the roof below the surface of any deposits.

The formation of iron sulphides is the result of a reaction between hydrogen sulphide (H$_2$S) and rust (Fe$_2$O$_3$). The reactions can be represented by the equations:

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow 2\text{FeS} \text{ (mackinawite)} + 3\text{H}_2\text{O} + \text{S}$$

$$3\text{FeS} + \text{S} \rightarrow \text{Fe}_3\text{S}_4 \text{ (greigite)}$$

Both mackinawite (FeS) and greigite (Fe$_3$S$_4$) can react with elemental sulphur to produce pyrite (FeS$_2$) giving a marked increase in pyrophoric reactivity:

$$\text{FeS} + \text{S} \rightarrow \text{FeS}_2 \text{ (pyrite)}$$

$$\text{Fe}_3\text{S}_4 + 2\text{S} \rightarrow 3\text{FeS}_2 \text{ (pyrite)}$$

Hence, the suggested overall route of conversion would be

hydrogen sulphide $\rightarrow$ mackinawite $\rightarrow$ greigite $\rightarrow$ pyrite

On exposure to air the pyrophoric iron sulphides react with oxygen liberating heat, e.g. for pyrite

$$4\text{FeS} + 7\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2 + \text{heat}$$

Walker et al. (1996) reported the results of an experimental study, which confirmed the nature of the above reaction pathways. Iron-sulphide compounds come in a variety of forms and the formation of specific compounds and phases depends on factors such as humidity, gas concentration and temperature. Trop-
ical climates should be particularly ideal for the formation of substantial amounts of potentially dangerous pyrite.

Pyrophoric iron sulphides can form in atmospheres containing oxygen concentrations of 3% or less. Dimpfl (1980) argued that the headspace of asphalt tanks often is oxygen deficient because smouldering fires deplete available oxygen. Davie et al. (1994) observed that bitumen deposits can undergo a smouldering reaction dependent on the availability of oxygen. This smouldering, sustained over a period of time, could lead to a depletion in the oxygen concentration in the storage tank and so contribute to conditions suitable for the formation of pyrophoric material.

Incidents of unknown origin have occurred during emptying of tanks, when manhole covers have been left open or raised by strong winds. In such situations with air ingress, smouldering deposits can reach high temperatures increasing the risk of fire.

The reactivity of the iron sulphide depends upon the type of iron oxide from which it was derived as well as upon the particle morphology. Experimental data have shown that the liberation of heat upon oxidation was higher for sulphides with smaller particle size and hence larger surface area than those with a larger size and smaller area (Walker et al. 1996). In another experimental study a mixture of pyrite and greigite produced sparks instantaneously on exposure to air(!)(Walker et al. 1997). The reactivity of greigite is utilized in the manufacture of Chinese export fire crackers which contain a mixture of chemicals containing 5-25% greigite (Walker et al. 1996).
4 Conclusion

The fire report holds no information if the Engelsberg tanker had an inert gas system at the time of the incident, or if present, if it was in use for the minor transfer. In all likelihood, the unloading of excess asphalt led to ingress of air through hatch openings where it met deposits of pyrophoric iron sulphides in the tank ullage. On exposure to air, the pyrophoric material ignited deposits of asphalt. The combustion generated convection flows that supplied additional air to the combustion zone, eventually intensifying the fire. This would seem to be the likely direct cause behind the 1977 fire.

There is no information as to why overfilling took place. Bearing in mind that refinery change of shifts took place at 07:00 poor shift hand over communication could be a contributing factor.

Figure 1 Undated photo of M/T Engelsberg -( IMO 6900305). Photo courtesy Christer Carlquist (www.shipphotos.se)
5 References


Gulf Oil (1977) *Rapport over brand M/T "Engelsberg", Stockholm*. OlP/kc (in Danish)
