ACCIDENT REPORT

MAIB

MARINE ACCIDENT INVESTIGATION BRANCH

Red Ensign Group

Cayman Maritime

INVESTIGATED BY THE MAIB ON BEHALF OF THE CAYMAN ISLANDS GOVERNMENT

Report on the investigation of the cargo tank explosion and fire on board the chemical tanker

Stolt Groenland

Ulsan, Republic of Korea

28 September 2019

SERIOUS MARINE CASUALTY REPORT NO 9/2021 JULY 2021

This investigation was carried out by the UK Marine Accident Investigation Branch (MAIB) on behalf of the Cayman Islands Government in accordance with the Memorandum of Understanding between the MAIB and the Red Ensign Group Category 1 registries of Isle of Man, Cayman Islands, Bermuda and Gibraltar.

Extract from

The Cayman Islands Merchant Shipping

(Marine Casualty Reporting and Investigation)

Regulations, 2018 – Regulation 4:

"The sole objective of a marine safety investigation into an accident under these Regulations shall be the prevention of future accidents through the ascertainment of its causes and circumstances. It is not the purpose of a marine safety investigation to determine liability nor, except so far as is necessary to achieve its objective, to apportion blame."

NOTE

This report is not written with litigation in mind and, pursuant to Regulation 22 of The Cayman Islands Merchant Shipping (Marine Casualty Reporting and Investigation) Regulations, 2018, shall be inadmissible in any judicial proceedings whose purpose, or one of whose purposes, is to attribute or apportion liability or blame.

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CONTENTS

FIGURES

TABLES

GLOSSARY OF ABBREVIATIONS AND ACRONYMS

2/O	-	Second officer
3/O	-	Third officer
ACA	-	American Cargo Assurance
AIS	-	Automatic identification system
CCR	-	Cargo control room
CDI	-	Chemical Distribution Institute
C/O	-	Chief officer
ERT	-	Emergency Response Team
HMD	-	Hexamethylenediamine
IBC Code	-	International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk
IMO	-	International Maritime Organization
Ineos	-	Ineos Styrolution America LLC
INTERTANKO	-	International Association of Independent Tanker Owners
iStow	-	iStow Tanker cargo stowage software
KMST	-	Korea Maritime Safety Tribunal
LPD	-	LPD Lab Services Limited
m	-	metre
m^3	-	cubic metres
mb	-	millibar
MARPOL	-	International Convention for the Prevention of Pollution from Ships
MCO	-	Marine Compliance Officer
OS	-	Ordinary seaman
OTK	-	Odfjell terminal in Ulsan, Republic of Korea
ppm	-	parts per million
PTZ	-	Phenothiazine
p/v	-	Pressure/vacuum
SDS	-	Safety Data Sheet
SHC	-	Specific Heat Capacity
SMS	-	Safety Management System
SOLAS	-	International Convention for the Safety of Life at Sea 1974, as amended

ST B503	-	Shore Tank 503
STCW	-	International Convention on Standards of Training, Certification and Watchkeeping for Seafarers 1978, as amended (STCW Convention)
Stolt	-	Stolt Tankers B.V.
t	-	tonne
TBC	-	4-tert-Butylcatechol
TEA	-	Triethanolamine
TSG	-	Tanker Safety Guide
UTC	-	Universal co-ordinated time
VCR	-	Voyage cargo report
VDR	-	Voyage data recorder
Voranol	-	Glycerol, propoxylated and ethoxylated
YMP3	-	Yeompo Quay, berth 3

TIMES: all times used in this report are UTC + 9 unless otherwise stated.

Permission requested via email. Image courtesy of Hannes van Rijn

Stolt Groenland

SYNOPSIS

On 28 September 2019, a cargo tank containing styrene monomer on board the Cayman Islands registered chemical tanker *Stolt Groenland* ruptured causing an explosion and fire. The tanker was moored alongside a general cargo berth in Ulsan, Republic of Korea and the Singapore registered chemical tanker *Bow Dalian* was moored outboard. The ignition of the styrene monomer vapour resulted in a fireball, which reached the road bridge above. Both vessels were damaged, and two crew suffered minor injuries. Fifteen emergency responders were injured during the fire-fighting, which lasted for over 6 hours.

The rupture of the styrene monomer tank resulted from a runaway polymerisation that was initiated by elevated temperatures caused by heat transfer from other chemical cargoes. The elevated temperatures caused the inhibitor, added to prevent the chemical's polymerisation during the voyage, to deplete more rapidly than expected. Athough the styrene monomer had not been stowed directly adjacent to heated cargo, the potential for heat transfer through intermediate tanks was not fully appreciated or assessed. Critical temperature limits had been reached before the vessel berthed under the road bridge in Ulsan. The tanker's crew did not monitor the temperature of the styrene monomer during the voyage, and therefore were not aware of the increasingly dangerous situaution.

A similar dangerous styrene monomer polymerisation incident had occurred a couple of weeks ealier on board another Stolt Tankers B.V. ship, *Stolt Focus*. The heat generated by the polymerisation process was noticed before the critical runaway temperature was reached. The styrene momomer cargoes on board both tankers was loaded at a similar time from the same tank in Houston and were exposed to similar environmental conditions. The incident on board *Stolt Focus* was not reported to the ship's Flag State or other masters in the Stolt Tankers B.V. fleet.

Following the accident, the Ministry of Oceans and Fisheries, Republic of Korea, prohibited ship-to-ship transfer operations for dangerous cargo on general cargo berths in Ulsan. Stolt Tankers B.V. took immediate action to ensure that the temperatures of all cargoes carried on board its ships were monitored and reported to its shore management. It also took steps to enhance crew awareness on the hazards of inhibited and heat sensitive cargoes. The company is developing technological and administrative initiatives to assist with the safe stowage and monitoring of heat sensitive cargoes.

A recommendation has been made to Stolt Tankers B.V. aimed at ensuring the wider marine chemical sector benefits from the lessons learned from the *Stolt Focus* incident and research initiatives that were carried out as a result of this accident. Recommendations have also been made to the Cayman Island Shipping Registry, the Chemical Distribution Institute and Plastics Europe (Styrene Producers Association). These are intended to assist in ensuring that the guidance provided in certificates of inhibitor and styrene monomer handling guides is consistent and achievable given the limitations of equipment and testing facilities on board ships.

SECTION 1 – FACTUAL INFORMATION

1.1 PARTICULARS OF *STOLT GROENLAND* AND ACCIDENT

SHIP PARTICULARS	
Vessel's name	*Stolt Groenland*
Flag	Cayman Islands
Classification society	Det Norske Veritas Germanischer Lloyd
IMO number/fishing numbers	9414072
Type	Chemical/products tanker
Registered owner	Stolt Tankers B.V.
Manager(s)	Stolt Tankers B.V.
Construction	Steel
Year of build	2009
Length overall	182.72m
Beam	32.24m
Gross tonnage	25881
Deadweight	43478
Minimum safe manning	17
Authorised cargo	Chemicals and oil products in bulk

VOYAGE PARTICULARS	
Port of departure	Kobe, Japan
Port of arrival	Ulsan, Republic of Korea
Type of voyage	International
Cargo information	Chemicals in bulk 27117 tonnes
Manning	25

MARINE CASUALTY INFORMATION	
Date and time	28 September 2019 at 1050
Type of marine casualty or incident	Serious Marine Casualty
Location of incident	Ulsan, Republic of Korea
Place on board	Cargo tanks and deck
Injuries/fatalities	2 crew suffered minor injuries (1 on board *Stolt Groenland* and 1 on board *Bow Dalian*). 15 shore workers/officials were also reported to have been injured. The severity of their injuries is not known
Damage/environmental impact	Toxic vapour released to atmosphere
Ship operation	Moored alongside
Voyage segment	Moored alongside
External & internal environment	Daylight. Air temperature: 24ºC Wind: Light airs. Humidity 93%
Persons on board	26

1.2 NARRATIVE

1.2.1 Passage and cargo discharge

Between 2 and 17 August 2019, *Stolt Groenland*, a Cayman Islands registered chemical tanker operated by Stolt Tankers B.V. (Stolt), loaded 20 different chemical cargoes from terminals in Texas, USA. Cargo was carried in 37 of the tanker's 39 cargo tanks for delivery in various ports in the Far East **(Table 1)**. Tanks 3 Port (3P), 7 Starboard (7S), 8P, 9P, 10P, and 11P contained heated cargoes. The temperatures of the cargoes in 3P and 7S were required to be maintained at between 40ºC and 45ºC, and the temperatures of the cargoes in 8P, 9P, 10P, and 11P (Hexamethylenediamine (HMD)), the last cargo to be loaded, had to be maintained at between 45°C and 50°C. The temperature of the HMD at loading was 61°C.

KEY:
Tank number
Liquid quantity/98%tank capacity (m³)
Chemical IMO name
Port of loading/discharge
Loaded/carriage temperature (ºC)

P = port | **C** = centre | **S** = starboard

Heated cargo | Styrene monomer

1P: 502/890 - Butyl cellosolve Texas City/Singapore 31/ambient	**1C:** 1272/1377- Acrylonitrile Point Comfort/Taiwan 29/ambient	**1S:** Adiponitrile - 870/890 Houston2/Ulsan 31/ambient
2P: 1259/1279 - Adiponitrile Houston2/Ulsan Odfjell terminal 32/ambient	**2C:** 1191/1326 - Acrylonitrile Point Comfort/Taiwan 29/ambient	**2S:** 1269/1279 - Ethylene dichloride Freeport/Ulsan 30/ambient
3P: 432/620 - Diglyceryl ether of bisphenol A Freeport/Ulsan 42/40-45	**3C:** 578/596 - Adiponitrile Houston2/Ulsan Odfjell 32/ambient	**3S:** 585/620 - Isobutyl acetate Houston2/Ulsan 31/ambient
4P: 264/352 - Dichloromethane Freeport/Ulsan 37/ambient	**4C:** 205/273 - Dichloromethane Freeport/Ulsan 35/ambient	**4S:** 262/352 - Dichloromethane Freeport/Ulsan 35/ambient
5P: 578/663 - Ethylene glycol monobutyl ether Houston2/Taiwan 33/ambient	**5C:** 587/610 - Adiponitrile Houston2/Ulsan Odfjell 31/ambient	**5S:** 443/663 - Toluene diisocyanate Houston1/Kobe 33/ambient
6P: 1973/2157 - Styrene monomer Houston1/Taiwan 17/ambient (inhibited - must not be heated)	**6C:** 1842/2085 - Styrene monomer Houston1/Taiwan 17/ambient (inhibited - must not be heated)	**6S:** 2110/2157 - Adiponitrile Houston2/Ulsan 31/ambient
7P: 916/1212 - Ethox polyhydric alcohol Houston2/Ulsan 39/ambient	**7C:** 528/1149 - Poly(2-8) alkylene glycol monoalkyl(C1-C6) ether Texas City/Singapore 31/ambient	**7S:** 462/1212 - Diglycidyl ether of bisphenol A Freeport/Ulsan 50/40-45
8P: 599/663 - Hexamethylenediamene (HMD) Houston2/Ulsan 61/45-50	**8C:** 494/610 - Triethanolamine Texas City/Ulsan 40/ambient	**8S:** 595/663 - Noxious liquid NF (5) NOS (Alfol 610) Houston2/Kobe 31/ambient
9P: 2092/2157 - HMD Houston2/Singapore 61/45-50	**9C:** 1953/2085 - Adiponitrile Houston2/Ulsan 34/ambient	**9S:** 1966/2157 - Styrene monomer Houston1/Taiwan 17/ambient (inhibited - must not be heated)
10P: 1124/1212 - HMD Houston2/Ulsan 61/45-50	**10C:** 1147/1149 - Glycerol, propoxylated and ethoxylated (Voranol) Freeport/Ulsan 32/ambient	**10S:** 955/1212 - Methyl methacrylate Houston2/Taiwan 32/ambient (inhibited - must not be heated)
11P: 314/324 – HMD Houston2/Singapore 58/45-50	**11C:** 299/329 – Ethanolamine Texas City/Kobe 33/ambient (55 maximum)	**11S:** 321/324 - Glycerol, propoxylated and ethoxylated(Voranol) Freeport/Ulsan 33/ambient
12P: 0/1383 - Empty	**12C:** 1346/1347 - Ethylene dichloride Freeport/Ulsan 32.5/ambient	**12S:** 0/1383 - Empty
13P: 1887/1889 - Ethylene dichloride Freeport/Ulsan 31/ambient	**13C:** 13C 1944/1954 - Ethylene dichloride Freeport/Ulsan 33/ambient	**13S:** 1886/1889 - Ethylene dichloride Freeport/Ulsan 32/ambient

Table 1: Cargo stowage on departure from Houston on 17 August

The cargoes also included 5245t of styrene monomer, loaded on 7 and 8 August, which was divided among cargo tanks 6P (1789t), 6 Centre (6C) (1671t), and 9S (1785t), to which a polymerisation inhibitor had been added (see Section 1.7.2). The tanker sailed for passage to Japan on 17 August.

Between 22 and 24 September, *Stolt Groenland*'s cargo tanks 5S, 8C (part cargo), 8S and 11C were discharged to barges while the vessel was at anchor off Kobe, Japan. The vessel then sailed to Ulsan, Republic of South Korea, where six tanks containing adiponitrile were discharged at the Odfjell terminal (OTK) on 26 and 27 September. During discharge on 26 September, the tanker's chief officer (C/O) handed over to his relief, who had arrived shortly after the vessel moored alongside. The off-going C/O departed the vessel at about 1500.

During the afternoon of 27 September 2019, *Stolt Groenland* shifted from the OTK to Yeompo Quay, berth 3 (YMP3) underneath the Ulsan Bridge **(Figure 1)**. The tanker moored starboard side to the quay and during the evening, a cargo of Voranol was discharged from cargo tanks 10C and 11S to *Stolt Voyager* via ship-to-ship transfer. On completion, *Stolt Voyager* moored ahead of *Stolt Groenland*.

The temperatures of the cargoes discharged in Kobe and at OTK recorded on the ullage reports are shown in **Table 2**. The attending cargo surveyor in Ulsan noticed that the temperature of the adiponitrile in 9C (48.8ºC) was elevated, but as it remained within the charterer's specified maximum temperature of 50ºC, he did not discuss this with the C/O and no action was taken. The distribution of the cargoes remaining on board *Stolt Groenland* following the discharges in Kobe and OTK is shown at **Figure 2**.

Date	Tank	Cargo	Place	Discharge Temperature
22-23 Sep	5S	Toluene	Kobe, Japan	33.2°C
22-23 Sep	8C (part cargo)	Triethanolamine (TEA)	Kobe, Japan	43.6°C
22-23 Sep	8S	ALFOL	Kobe, Japan	39.1°C
22-23 Sep	11C	MEA	Kobe, Japan	48.2°C
26-27 Sep	1S	ADIPONITRILE	OTK, Ulsan	27.2°C
26-27 Sep	2P	ADIPONITRILE	OTK, Ulsan	30.0°C
26-27 Sep	3C	ADIPONITRILE	OTK, Ulsan	29.8°C
26-27 Sep	5C	ADIPONITRILE	OTK, Ulsan	30.5°C
26-27 Sep	6S	ADIPONITRILE	OTK, Ulsan	31.9°C
26-27 Sep	9C	ADIPONITRILE	OTK, Ulsan	48.8°C
27 Sep	10C	VORANOL	YMP3, Ulsan	46.0°C
27 Sep	11S	VORANOL	YMP3, Ulsan	38.4°C

Table 2: Temperatures of cargoes discharged in Kobe and Ulsan

Satellite image courtesy of Google Maps

Figure 1: Ofdjell terminal and Yeompo Quay, Ulsan

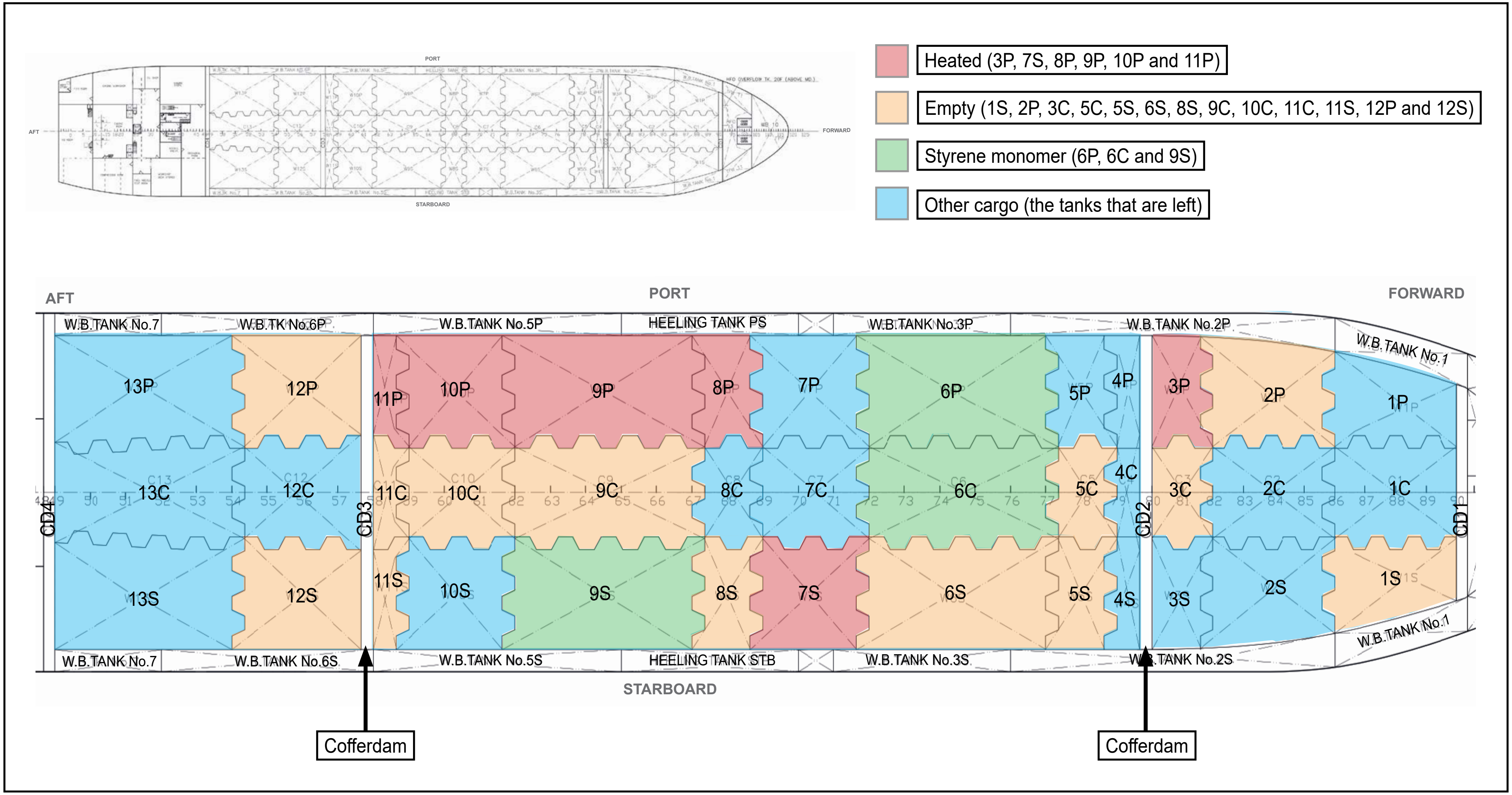

Figure 2: Cargoes remaining following discharge in Ulsan

1.2.2 Explosions

At about 0600 on 28 September, the Singapore registered chemical tanker *Bow Dalian* was secured alongside *Stolt Groenland*'s port side. The purging of *Bow Dalian*'s cargo tanks with nitrogen supplied from shoreside vehicles was then started in readiness for a ship-to-ship cargo transfer with *Stolt Groenland*.

At 1043, vapour started to release from the pressure/vacuum (p/v) relief valve for *Stolt Groenland*'s 9S cargo tank **(Figure 3)**. About 2 minutes later, the tank's high-level alarm (indicating that the level in 9S cargo tank had reached 95%) activated the warning siren and strobe light on the bridge front. The warning indicators were noticed by the ordinary seaman (OS) on gangway watch, and he immediately notified the third officer (3/O), the on-watch deck officer, via hand-held radio. The 3/O was working in the master's office and went to the unmanned cargo control room (CCR) to investigate.

The OS's radio transmission was also heard by the C/O, and he joined the 3/O in the CCR. Shortly afterwards, the high-high-level siren on the bridge front sounded, indicating that the level in 9S cargo tank had increased to 98%. The alarm was again reported by the OS. The C/O and 3/O saw from the cargo monitoring system that the pressure inside 9S cargo tank was 1340mb, and observed it rise quickly to 2000mb.

At 1050, two explosions occurred in rapid succession in way of the vessel's cargo manifold **(Figure 4)**. The second explosion ignited the released styrene monomer vapour **(Figure 5)** and the resulting fireball passed very close to the road bridge above the quay **(Figure 6)**. It also ignited vapours released from the 9S and 9C p/v valves.

1.2.3 Emergency response

Stolt Groenland

On board *Stolt Groenland*, the force of the second explosion blew the gangway watchman over the starboard side guardrails on the main deck. The OS initially held on to one of the rails, but he was soon forced to let go due to the heat from the fire. He fell into the water between the quay and the vessel, but he was able to climb over a fender and on to the quay.

The C/O activated the fire alarm and the tanker's crew mustered at their fire stations. The C/O also activated the deck foam monitor system and directed the port monitor toward the cargo manifold. The 3/O did likewise with the starboard monitor. However, the master soon ordered everyone to the lifeboat station on the boat deck due to the intensity of the fire and the thick black smoke. The crew used the freefall lifeboat to abandon the tanker.

Bow Dalian

Following the explosions, *Bow Dalian*'s C/O activated the vessel's emergency alarm and the deck foam fire extinguishing system. He and the master also directed the monitors toward *Stolt Groenland*'s main deck and cargo manifolds. The crew then abandoned ship via a rope ladder on the vessel's port side on to Korea Coast Guard vessels, which had arrived to assist.

Figure 3: CCTV still showing vapour release from 9S p/v valve

Figure 4: CCTV still showing tank rupture and vapour release

Figure 5: CCTV still showing vapour ignition

Image courtesy of @803_Gorani (Twitter)

Figure 6: Fireball at Ulsan bridge

Stolt

Stolt was informed of the explosions and fire on board *Stolt Groenland* by a marine compliance officer (MCO) who was on board *Stolt Voyager*, and immediately activated its Emergency Response Team (ERT) in the Netherlands. The ERT communicated with its MCO via telephone and 'WhatsApp messenger' and established that *Stolt Groenland*'s crew were safe. At 1528, the ERT were informed of a further explosion toward the tanker's accommodation. However, at 1612, it received a report that the fire had dampened down and that no flames were visible. Shortly afterwards, the fire was reported to have been extinguished, although there was still smoke in the accommodation.

Stolt's protection and indemnity insurers, Gard, appointed the Netherlands based salvors Ardent, to assist Stolt's emergency response team. It also e-mailed its fleet to check styrene monomer cargoes that were being carried. This was later backed up by fleet *Flash Report no.2019/08* highlighting the precautions required when styrene monomer is carried.

Local emergency services

Local fire brigade shore appliances arrived at YMP3 at 1101 and started to fight the fire. Korea Coast Guard fire-fighting tugs and launches assisted and towed *Bow Dalian* to a berth clear of Yeompo. A total of 726 emergency responders participated in the firefighting and rescue operations, with 117 fire-fighting appliances being deployed to the scene. A total of two ships' crew and 15 emergency responders suffered injuries and were taken to hospital for observation or treatment.

1.3 ENVIRONMENTAL CONDITIONS

During the cargo loading in Texas and during passage in the Caribbean, the average air and sea temperatures experienced by *Stolt Groenland* were about 30°C, peaking at 37°C air temperature during the day. These averages reduced to about 25ºC during the passage across the Pacific Ocean.

In Kobe, the sea temperature was 26ºC and the maximum and minimum air temperatures were 30ºC and 28ºC. In Ulsan, the sea temperature was 24ºC with maximum and minimum air temperatures of 25ºC and 19ºC.

1.4 ON-SITE INVESTIGATION

On 28 September, the Maritime Authority of the Cayman Islands requested the MAIB investigate this accident in accordance with the International Maritime Organization (IMO) Casualty Investigation Code (IMO Resolution MSC 255(84)). During the on-site investigation in Ulsan, the MAIB was assisted by the Korea Maritime Safety Tribunal (KMST). Access to *Stolt Groenland* was controlled by the Korea Coast Guard and restricted by the toxicity of the atmosphere on board.

On 3 October, with the co-operation of *Bow Dalian*'s owners and the Transport Safety Investigation Bureau of Singapore, MAIB inspectors and KMST staff visited *Bow Dalian* in Ulsan. The tanker's weather decks and accommodation block were spattered with burned residues **(Figure 7)**. A sample of residue **(Figure 8)**, and the overalls **(Figure 9)** from a crewman who had been on deck during the period of vapour release from 9S's p/v valve, were removed for analysis (see Section 1.20).

On 7 October, the analysis of samples of styrene monomer taken from *Stolt Groenland*'s cargo tanks 6C and 6P indicated that the concentrations of the inhibitor 4-tert-Butylcatechol (TBC) were 8 parts per million (ppm) and 7ppm respectively. The following day, MAIB inspectors were allowed access to the vessel. However, the presence of hazardous chemicals and fire damage limited the inspection to the main deck primarily. A further inspection on 12 November was co-ordinated by the Korea Coast Guard and the KMST. These inspections, and inspections conducted by or on behalf of Stolt, confirmed that the heating coils in 9C and 9S were closed and blanked **(Figure 10)**, and that vapours released from the p/v valves for 9S and 9C had ignited.

1.5 DAMAGE

A large hole was found in *Stolt Groenland*'s main deck in way of cargo tank 9S and its common bulkhead with cargo tank 9C **(Figures 11** and **12)**. The access hatch cover to 9S had also been blown off **(Figure 13)**. The manifold area was fire damaged to varying degrees, and the midships deckhouse was burned out **(Figure 14)**.

The tanker's accommodation block sustained extensive internal fire damage **(Figure 15)**. The deck between the technical room and the CCR had collapsed, and both spaces were burned out. Heat and smoke had also penetrated the bridge and damaged much of its equipment. Other than broken windows, many of which were broken by firefighters during the emergency response, external damage to the front of the accommodation block was minimal **(Figure 16)**.

1.6 ONBOARD RECORDS

Cargo-related records and voyage related records such as 'noon reports' were available on 'Veslink', a networked system that was used on board *Stolt Groenland* to store data and to communicate with interested parties ashore. In addition to mandated information, *Stolt Groenland*'s voyage data recorder (VDR) recorded cargo tank levels, volumes, temperatures, and liquid densities.

All cargo-related records (digital and paper) that were held in the CCR and the cargo samples stored in the midships deckhouse were destroyed in the fire. However, the cargo temperature data from 0001 (UTC) on 30 August to 0150 (UTC) on 28 September **(Figure 17)**, the time range of the data that was available, was recovered from the VDR.

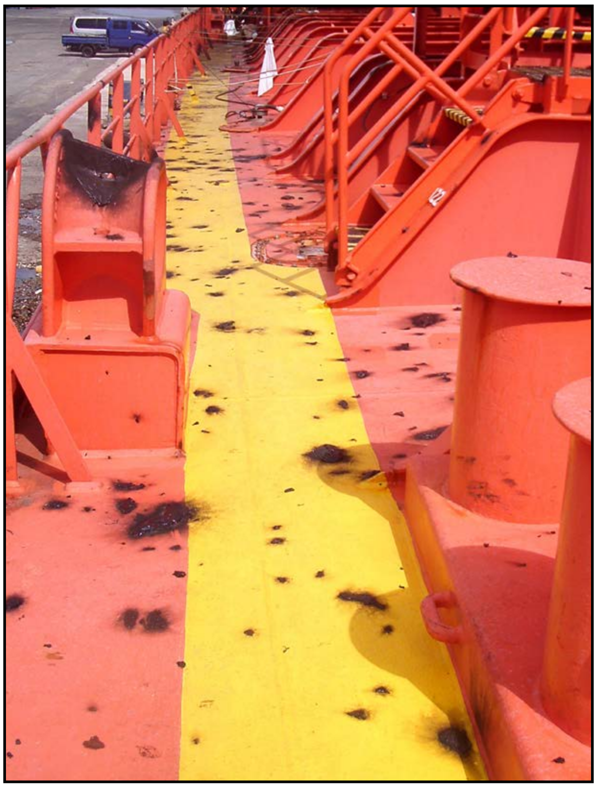

Figure 7: *Bow Dallian* main deck with burned styrene deposits

Figure 8: Styrene residue sample

Figure 9: Overalls from *Bow Dallian* crewman

1.7 STYRENE MONOMER

1.7.1 Description

Styrene monomer (also known as ethenylbenzene, phenylethylene, phenylethene, vinylbenzene, or cinnamene) is an aromatic hydrocarbon and a building block of the plastics industry. It is commonly used in the manufacture of a variety of plastic, rubber and polystyrene products. Over 30 million tonnes of styrene are produced annually, much of it transported by sea to plastics production plants.

Styrene monomer is a colourless, transparent liquid under ambient conditions and has a distinctly sweet odour. It is a volatile and flammable substance with a flashpoint of 32ºC. Its boiling point is 145ºC and its auto ignition temperature is 490ºC.

The harmful effects of styrene monomer include severe irritation to eyes and mucous membranes, as well as gastrointestinal effects. Chronic exposure to styrene monomer leads to central nervous system dysfunction, such as headache, fatigue, weakness, depression, hearing loss and nerve damage.

Figure 10: 9S heating control valves

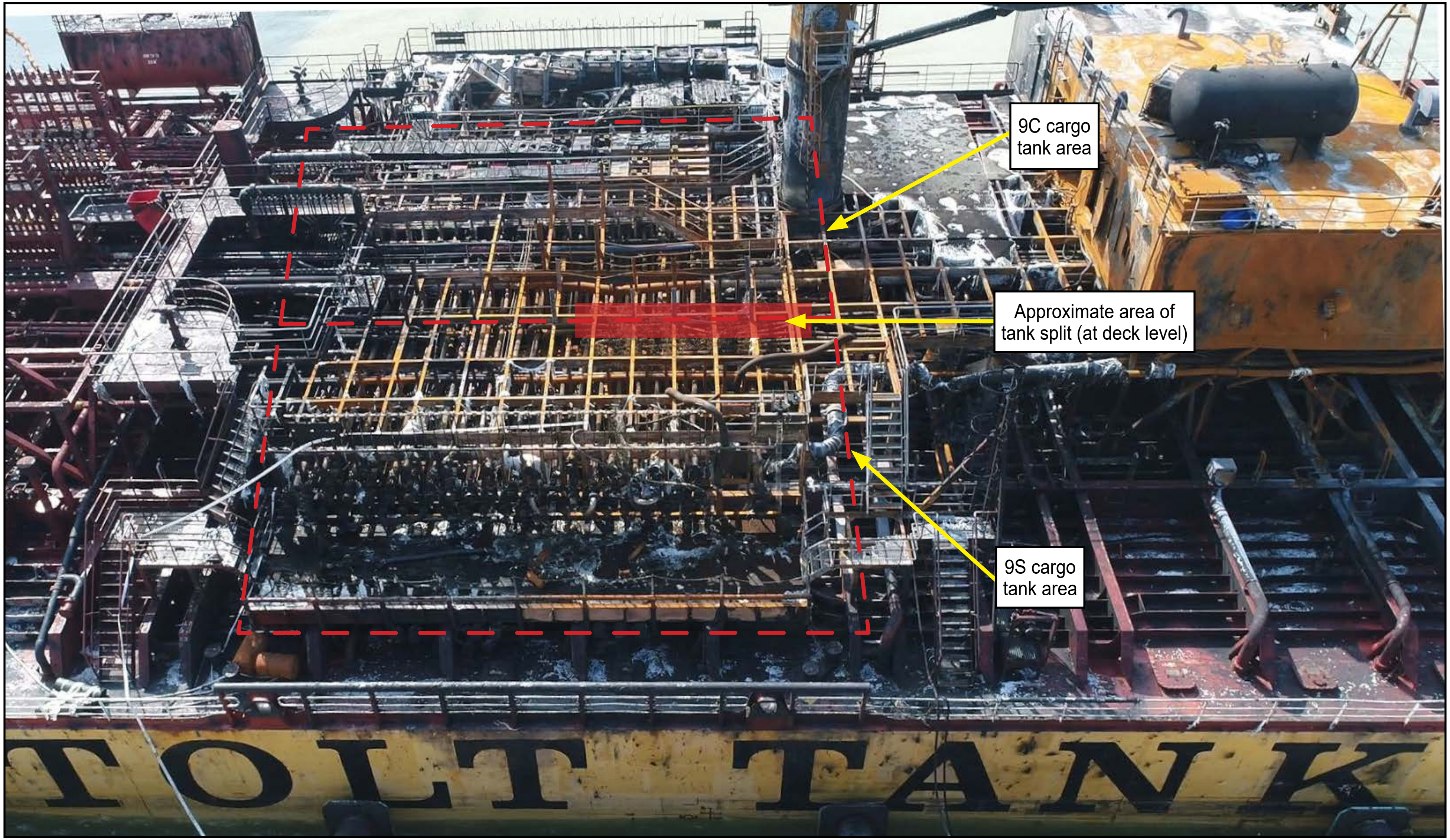

Figure 11: Aerial view of main deck and location of 9S

Figure 12: 9S tank rupture


Figure 13: 9S access hatch

Figure 14: Midships deckhouse

Figure 15: Accommodation interior

Figure 16: Accommodation front

1.7.2 Polymerisation

Polymerisation is a chemical reaction, or process in which a monomer or a mixture of monomers is converted into a polymer such as polystyrene. Styrene polymerises slowly at normal ambient temperatures but very rapidly at elevated temperatures. It can be accelerated by heat, the lack of dissolved oxygen, the lack of a polymerisation inhibitor, and when contaminated by oxidising agents and most halides.

The polymerisation process is exothermic and, if the resulting heat is not removed, the bulk styrene temperature may rise to a level at which polymerisation is self-sustaining and very rapid. This is referred to as 'runaway polymerisation' and will usually be initiated by temperatures above 65°C. During a runaway polymerisation, the cargo will expand causing pressure to increase to the point that vapour is released from tank vents or p/v valves. In some cases, the resulting build-up of pressure is sufficient to rupture the tank.

1.7.3 Polymerisation inhibitors

To prevent polymerisation during storage and transportation, an inhibitor must be added. TBC, the most commonly used polymerisation inhibitor, is a solid but is often mixed with methanol to produce a liquid before adding to styrene monomer. In shore storage facilities, TBC is added to styrene monomer through dosing systems. For the marine transportation of styrene monomer in bulk, the TBC is added to the bottom of a cargo tank before loading. TBC should be stored in non-reactive, light resistant containers at ambient temperature. It is not known to have a limited shelf life.

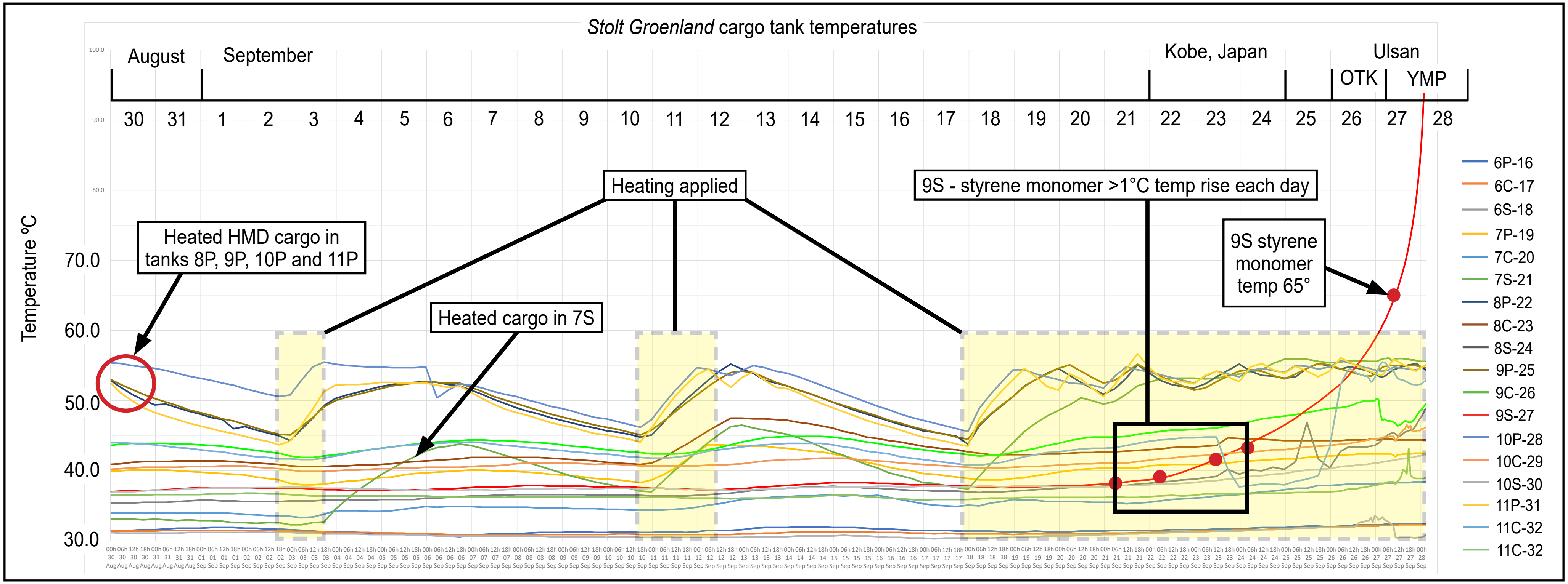

Figure 17: Cargo temperatures recorded on the VDR

The TBC level must be maintained within a specified concentration range, typically between 10-15ppm, to prevent polymer formation. The presence of dissolved oxygen is required for the inhibitor to function properly and it is the inhibitor that controls oxygen depletion. Where ambient temperatures are likely to exceed the flash point of the cargo, it might be desirable to use a nitrogen blanket to minimize the risk of fire or explosion. However, the atmosphere above styrene monomer should contain 3% to 8% (volume) of oxygen to maintain inhibitor effectiveness and therefore avoid polymerisation. Whether stored under air or a nitrogen blanket, the inhibitor concentration is depleted more rapidly at elevated temperatures. Consequently, styrene monomer is usually kept below 30°C when transported and below 20°C in storage tanks ashore.

1.8 CARGO SYSTEM

Stolt Groenland was built in 2009 and was one of six sister vessels. The tanker had 39 integral cargo tanks of varying capacities, which were separated into three fore to aft sections by two transverse cofferdams. The tanks in the fore and aft sections (tanks 1-3 and 12-13) were constructed of zinc coated mild steel; the mid-section (tanks 4-11) was of solid duplex stainless steel construction. The tanks' bulkheads were corrugated. All stainless steel tanks were fitted with heating coils, capable of maintaining a temperature of up to 85°C. The heating medium was water, and the system was controlled manually via valves on deck.

Each cargo tank was independent and had its own pump and pipeline arrangement. The tanks were protected against over and under pressures by individual p/v relief valves, which were situated at two vent stacks on the main deck. The lifting pressure of the p/v valves was 206mb.

Tank liquid levels were measured by a closed radar system, and tank pressures and temperatures by internal sensors. The temperature sensors were located at low and middle levels in each tank. Data from the radar and tank sensors was monitored via an *Ariston* computerised cargo monitoring system in the CCR (with a slave display on the bridge). The data was also fed to the vessel's *CargoMax* stability computer. The information displayed by the Ariston system on the cargo monitor screens was determined by user preference. The system could be configured to show individual tanks or groups of tanks. The user was also able to set cargo level, temperature and pressure alarms for each tank.

Stolt Groenland's crew could not test or monitor for TBC concentration, oxygen or polymer levels in the styrene monomer cargoes. These values could only be determined in shore laboratories.

1.9 LOADING IN HOUSTON

1.9.1 Planning and documentation

The cargo stowage plan for the loading between 2 and 17 August was first sent to *Stolt Groenland* by the tanker's shore-based ship operator (see Section 1.11) on 19 July. Inconsistencies between the voyage cargo report (VCR) and the vessel's *iStow Tanker* (iStow) cargo stowage computer, were raised by the C/O. These were subsequently addressed by the ship operator, and the plan was re-issued. Following further iterations of the plan, during which the intended stowage of the styrene monomer cargo was amended from cargo tanks 6P, 6C, and 10S, to 6P, 6C and 9S, a final iStow file and VCR was issued by the ship operator on 1 August. The plan was checked and agreed by *Stolt Groenland*'s C/O and approved by the tanker's master.

The VCR listed the nominated cargoes for the forthcoming voyage. It also cross-referenced the bill of lading number with the chemical name, quantity, ports of loading and discharge, cargo-handling requirements, and safety references. It included:

430 STYRENE MONOMER
Generic specs:

HANDLING	*UPDATED 10 JUL 18 FOR SHELL REVISION 9 DATED 01 APR 18*
HEAT ADJ	*NO HEATED CARGO TO BE STOWED ADJACENT.*
IMO	*Ships carrying this product must be provided a Certificate of Protection (Inhibitor Certifcate) from the shipper in order to comply with the requirements of 15.13.3.* *1) Name and amount of additive/inhibitor* *2) If additive is Oxygen dependent* *3) Date additive was added to cargo and duration of effectiveness* *4) Temperature limitations affecting effective lifetime of additive* *5) Action that needs to be taken should voyage exceed effective lifetime of additive or a statement concerning the Oxygen level required if the exclusion of air method is being used to stop oxidization as per 15.13.4.* *If an Inhibitor Certificate is to be issued it MUST state if the Inhibitor is Oxygen Dependent, or not, and if it is Oxygen Dependent it MUST state the Oxygen level which will allow the inhibitor to be effective.* *If you do not receive this documentation please alert your Ship Operator as soon as possible.* *IBC Code 15.19.6 High Level alarm in cargo tank* *IBC Code 16.6.1 NO ADJACENT HEAT as this cargo can potentially go into a state of POLYMERIZATION, DECOMPOSITION. THERMAL INSTABILITY OR EVOLUTION OF GAS* *IBC Code 16.6.2 HEATING COILS IN TANK(S) loading this cargo MUST BE BLANKED OFF*
IMO Name	*STYRENE MONOMER*
INCOMPAT	*Polymerization catalysts. Strong oxidizing agents.*

The Shell document referred to in the VCR was their Cargo Handling Sheet for styrene monomer, which was intended for use by vessels chartered by Shell Chemicals. It included:

> *Loading Temperature Range: 13 – 23 °C / 55 – 73 °F*
>
> *Transit Temperature Range: Ambient*
>
> *Discharge Temperature Range: Ambient*

Maximum Heating Coil Temperature: Blanked Off

Adjacent Maximum Cargo Temperature: 35°C

Note 1: This product is heat sensitive, self-reactive and inhibited.

Note 2: Shell Chemical SM is generally inhibited with Para-tertiary Butyl Catechol (p-TBC), typically at 10-20 ppm or more, depending on duration of voyage. Where required to add additional inhibitor to a loaded tank of styrene, this should be done using closed equipment. If the equipment is not available and there is a requirement to add inhibitor, the local Chemical MTA should be consulted.

DAILY LOG: During the voyage the vessel shall maintain a daily log of the following and, upon request, send the log to the responsible Shell Chemicals Charterer:

1. *cargo (Styrene) temperature*
2. *adjacent cargo temperature*
3. *air and sea water temperature*

If during the voyage any of the following is observed, the responsible Shell Chemicals Charterer shall be notified immediately:

- *1 °C rise of cargo (styrene) temp per day, over 3 consecutive days*
- *> 2 °C rise of cargo (styrene) temperature within any 24 hours*
- *Cargo temperature at any time raises above > 30°C*
- *O_2 content in cargo (styrene) tank ≤4% by volume, when inerted*

After completion of cargo (Styrene) discharge the vessel shall provide a copy of the daily log of temperature/pressure/O2 content to the responsible Shell Chemicals Charterer.

Due to risk of polymerization, Styrene should not be carried in tanks serviced by a cargo pump room.

1.9.2 The cargo

The styrene monomer carried on board *Stolt Groenland* was supplied by Ineos Styrolution America LLC to the LBC Terminal in Houston, USA. The cargo was pumped from shore tank B503 (ST B503) to the tanker during 7 and 8 August 2019 and was designated as cargo *OBL430*. The charterer on the Bill of Lading was Samsung C&T Corporation.

Prior to loading, the cargo tanks 6P, 6C and 9S had passed wall wash tests and visual inspections conducted by a cargo surveyor from American Cargo Assurance (ACA), and a preloading acceptance certificate was issued.

During the afternoon of 7 August, the ACA cargo surveyor and *Stolt Groenland*'s C/O completed a preloading checklist and exchanged cargo documentation which included a safety data sheet (SDS) for styrene monomer (stabilised) issued by Ineos Styrolution. Shortly afterwards, the surveyor carried out a final visual check of 6P, 6C, and 9S and then poured 3 US gallons (11.4 litres) of liquid inhibitor TBC into each of the tanks through their respective cleaning hatches. The addition of the inhibitor was witnessed by a terminal representative. No inhibitor was provided to the tanker's crew to carry on board during the voyage.

The loading of the styrene monomer started at 1735 (UTC-5) on 7 August from one shore cargo hose. The hose was connected to the tanker's manifold via a splitter spool piece connected to tanks 6P and 6C. A cross-connection on the manifold also enabled the simultaneous loading of cargo tank 9S. The temperature of the styrene monomer stored in ST B503 was 13ºC.

Between 0146 and 0340 on 8 August, pumping was stopped while awaiting the results of the shoreside testing of styrene samples from the cargo tanks. The analysis did not identify any issues, and loading was completed by 1520. The observed temperatures of the styrene monomer in *Stolt Groenland*'s cargo tanks shortly after the loading was completed ranged between 16.7 and 17.2ºC.

At 1550, the ACA surveyor sealed the access and cleaning hatches for cargo tanks 6P, 6C and 9S. He then issued a *Certificate of Inhibitor* **(Figure 18)**, which was signed by the attending terminal representative and *Stolt Groenland*'s C/O. This stated that the ideal temperature for the cargo was 60-85ºF (15.5-29.4ºC) and that if these conditions were exceeded, the cargo should be monitored for the inhibitor level and polymerisation, adding additional inhibitor as needed.

1.9.3 Styrene and inhibitor mixing

The TBC liquid added to the tanks before cargo loading was thick and viscous, and its mixing with the styrene monomer relied on the agitation achieved during the loading process and the sloshing caused by vessel movement on passage. The partial agitation caused by the flow of the styrene monomer cargo as it loads into the tank was not sufficient to adequately mix the TBC with the styrene cargo. For this reason, TBC concentration tests, done both during and immediately after loading were prone to inaccuracy, and were therefore not undertaken. Instead, calculations were conducted and the notation 'adjusted to XX ppm' was used in the shipment analysis reports. This process was standard industry practice for styrene bulk transportation by sea.

1.9.4 Styrene sampling

During the loading of the styrene monomer, the ACA surveyor took 1 US pint (0.47 litre) samples of the cargo on opening ST B503 from the dock-line, the cargo manifold and the 6P, 6C, and 9S pump stacks. The surveyor also took samples from each tank at the first foot[1] and the final levels. The surveyor passed the samples to the C/O and these were then stored in the midships deck housing.

The surveyor also sent a sample from ST B503, and cargo tank samples to an Ineos laboratory ashore for testing. The samples from 6P, 6C and 9S were combined for both the first foot and final levels, and were tested as composite samples.

[1] The 'first-foot', or about 30cm, of loaded cargo was sampled to check if the cargo pipeline system was clean.

ACA

AMERICAN CARGO ASSURANCE

CERTIFICATE OF INHIBITOR

(Styrene Monomer)

Vessel:	Stolt Groeland	Stowage:	6P,6C,9S
Facility / Port:	LBC Houston	Supplier:	Styrolution
Product:	Styrene Monomer	Surveyor:	[redacted]
Client Ref#:	8001158394	ACA Ref#:	H-191003

We confirm that the cargo loaded as described above has been properly inhibited as follows:

Inhibitor Type: **TBC** **Liquid** Target: **17** PPM

Nominated Quantity: 5,250 M/T Added: **9** **Gallons**

Date Added: **8/7/2019**

Days Effective: **60 - 90 DAYS**

Inhibitor Statement:

Inhibitor is oxygen dependent. If a nitrogen purge is required prior to loading, the oxygen content of the receiving tanks should be lowered to a level between 5% to 8%.

The minimum oxygen level to maintain the integrity and effectivness of the inhibitor is 5%.

Ideal temp for this cargo is 60-85F.

Loading Styrene next to heated cargos is not recommended

If these conditions are exceeded, the cargo should be monitored for the inhibitor level and polymerization, adding additional inhibitor as needed.

Check With Client Before Adding Supplied Inhibitor

Emergency contact numbers

ACA [redacted]

Issued By: [redacted]

On behalf of American Cargo Assurance

Witness: [redacted]

Terminal Personnel

Vessel: [redacted]

Chief Mate

Figure 18: Certificate of Inhibitor

The *Styrene Shipment Analysis* report concerning the composite final sample **(Figure 19)** stated that the TBC concentration was adjusted to 17ppm and the Certificate of Inhibitor stated that the 'Days Effective' was 60-90 days. The concentration level was a calculation based on the TBC concentration in ST B503 (11.3ppm) and the amount of inhibitor that was added into the tanks prior to loading.

1.10 CARGO TEMPERATURE CHANGES DURING THE VOYAGE

Stolt Groenland's styrene monomer cargo was due to be discharged in An-Ping, Taiwan about 56 days after it was loaded in Houston. The VDR provided hourly cargo temperature records for the 30-day period prior to the explosion **(Figure 17)**. At 1200 (UTC) on 30 August the recorded temperatures of the styrene monomer in 6P, 6C and 9S were 31.5, 31.4 and 37.2°C respectively. The temperatures of the HMD in 9P and the adiponitrile in 9C were 51.5 and 43.9°C respectively.

The temperature variations recorded in cargo tanks 8P, 9P, 10P and 11P showed that the HMD had been routinely heated to about 55°C and then allowed to drop to about 45°C. This was achieved by opening and closing the heating coil valves; it typically took about 2 days to heat the HMD and 5 days to for its temp to drop. This weekly heating cycle resulted in temperature variations of about 2.5°C in 9C and 0.5°C in 9S.

On 18 September, the heating coil valves for 8P, 9P, 10P and 11P were opened and the temperature was increased to about 55°C, where it was maintained ahead of the planned cargo discharge programme. At 1200 (UTC) on 18 September, the temperatures of the cargoes in 8S, 9S, 10S and 11S were 37, 37.7, 37.8 and 36.1°C respectively. The subsequent daily 1200 (UTC) temperatures of the starboard tanks are shown in **Table 3**.

Dates	8S midday temperature (°C)	9S midday temperature (°C)	10S midday temperature (°C)	11S midday temperature (°C)
19 Sept	37.3	37.6	37.8	36.2
20 Sept	37.7	37.9	37.7	36.2
21 Sept	37.9	38.4	37.9	36.2
22 Sept	38.5	39.4	38.1	36.5
23 Sept	39.4	41.8	38.6	36.7
24 Sept	40.1	44.9	39.3	36.8
25 Sept	46.0	48.9	40.1	36.9
26 Sept	43.4	54.5	40.7	37.4
27 Sept	44.9	66.7	41.6	38.7

Table 3: Midday temperatures for tanks 8S, 9S, 10S and 11S between 19 and 27 September 2019

The temperature of the styrene monomer in 9S rose by 1°C on three consecutive days between 21 and 24 September and rose by 2.4°C between 22 and 23 September. It reached 65°C at about 1000 (UTC) on 27 September and 100.8°C immediately before the explosion.

INEOS STYROLUTION Bayport	Styrene Shipment Analysis	Date Prepared: 8/8/2019 Time In: 17:01

Customer: Samsung HOUSTON, TX	Status: Pass	Ship/Barge Name: STOLT GROENLAND Shore Tank: B503

Delivery Number: 8001158394 Customer PO: SAM07262019-SM-001 July SM 2019	Comments: None

TEST / TEST METHOD	SPECIFICATIONS	FINAL SAMPLE
Color, Pt-Co Scale / ASTM D5386 , max	15	7
TBC, mg/kg (Tank 10-15) / ASTM D4590	(Target 17)	Adjusted to 17
Polymer, mg/kg / ASTM D2121 , max	10	1.0
Aldehydes, ppm, max / ASTM D2119, max	100	50
Peroxides, ppm, max / ASTM D2340, max	50	6
Appearance	Bright & Clear	Pass
Water, ppm / ASTM D7375		87
Weight % Purity by GC / ASTM D5135		
Ethylbenzene	0.010	0.007
Styrene, min	99.90	99.929
Xylenes		0.001
Cumene		0.007
n-Propylbenzene		0.004
α-Methylstyrene		0.027
Phenylacetylene		0.0128
Others		0.0122

For questions concerning this analysis, call [redacted]

Approved by: [redacted]

The specifications listed may be more restrictive than customer requested to insure quality and maximum product performance. Benzene is less than 0.0001 weight % by GC method ASTM D5135 (modified).

FORM QA5A077 Seq No: 851090 COA ID: 377683 *Date form printed from network: 8/9/2019 at 12:46 AM*

Figure 19: Final sample analysis results

1.11 CREW

1.11.1 General

Stolt Groenland's crew comprised 10 officers and 15 ratings. The officers were Russian nationals and the ratings Filipino nationals. All crew held the appropriate STCW[2] certification, including the chemical tanker basic training endorsement. The length of contract for the officers was 4 months. Two of the ratings were pumpmen, whose duties primarily concerned cargo operations.

The master, senior officers and deck officers also had completed the STCW chemical tanker advanced training (see Section 1.15.2) within the last 5 years in accordance with Regulations V/1-1 and V/1 – 2. They viewed styrene monomer as a comparatively benign cargo when inhibited, and none had previously experienced problems with its carriage.

1.11.2 Master

Stolt Groenland's master had worked for Stolt since 1999, serving on a variety of ships. He had been a C/O for 5½ years and was promoted to master in 2009. Since 2016, he had been *Stolt Groenland*'s regular master, and prior to that he had served on its sister ships. The master last joined *Stolt Groenland* on 14 August 2019.

1.11.3 Chief officer (Ulsan)

The C/O that joined the vessel in Ulsan started his career with Stolt in 2008 and had remained with the company throughout. He was promoted to second officer (2/O) in 2011, and to C/O in 2016. It was his fifth contract on *Stolt Groenland*, and he had also served on the vessel's sister ships.

1.11.4 Chief officer (loading and voyage)

The C/O that oversaw the cargo loading operation and completed the passage to Ulsan started his sea career as cadet in 2006 and worked on board oil tankers before joining Stolt as a 3/O in 2011. He was promoted to 2/O in 2012 and to C/O in 2017. The C/O had served as C/O on *Stolt Groenland* three times, usually with the same master and crew. He last joined the tanker in June 2019.

1.11.5 Voyage routines

On passage, *Stolt Groenland*'s crew carried out watchkeeping duties and routine maintenance. The C/O worked days, supervising the deck crew and the pumpmen as well as completing administrative tasks and inspections. The C/O was responsible for monitoring the cargo and ensuring that the heated cargoes remained within the temperature ranges specified on the VCR. The adjustment of the heating controls to keep the heated cargoes within these parameters was delegated to one of the pumpmen. The second pumpman assisted with monitoring and maintaining pressures in the cargo tanks that had been protected with a nitrogen blanket.

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[2] International Convention on Standards of Training, Certification and Watchkeeping for Seafarers 1978, as amended (STCW Convention)

1.12 CARGO MANAGEMENT ASHORE

Stolt was the world's largest operator of chemical tankers, with a fleet of over 100 vessels. Cargo operations were co-ordinated from its main operations centres in Rotterdam, Houston and Singapore, and each vessel had a nominated ship operator who was responsible for cargo allocation and cargo loading and discharge programmes. The ship operator was the master's shore-based point of contact for cargo-related issues.

Stolt Groenland's ship operator was based in Houston and was typically responsible for between four and five tankers at any one time. The ship operator had 23 years' experience in the shipping industry and had worked for Stolt as a ship operator for 4 years, having initially completed 6 months' on the job training under the supervision of an experienced manager.

The ship operator used the iSTOW software, supported by Stolt's 'Chemscan' database, to plan cargo stows. The database contained details of each chemical cargo, including temperature and nitrogen requirements, and enabled the iSTOW programme to identify inconsistencies in stowage plans related to aspects such as heated and cooled cargoes, heat in adjacent tanks, and cargo quality requirements. As a result, the iSTOW software informed the ship operator of the mix of cargoes a ship was able to carry.

The user guide for iSTOW described the system as:

> *…a computerized system that assists ship operators in the cargo stowing process. The system provides a "click, drag, and drop" feature for assigning of cargoes from a list to a cargo tank. STOW makes no attempt to stow the ship for the ship operator. Instead, it is a tool to assist the ship operator in the stow process and to alert them when any rules or regulations are violated.*
>
> *The system records stow changes made by the ship operator, sends and prints stow plans (including versions for last three cargoes and tank condition). Once the Stow Plan has been completed, the ship operator can ask the system to perform checks of the current Stow Plan. These checks use a combination of information from the Stolt CHEMSCAN Database and IMOS[3]. For example, if one of our customers has requested that we carry their cargo in a stainless-steel tank and that the adjacent cargoes are not heated above a certain temperature, the system will detect if there is a potential problem and alert the ship operator. Other checks are US Coast Guard compatibility, commingling, and last cargo restrictions. Additional checks are scheduled to be developed in compliance with changes in rules and regulations.*

On completion of verifying an intended cargo stowage plan in iSTOW, the ship operator forwarded the iSTOW file and the VCR to the vessel to check the viability of the stowage plan regarding factors including cargo compatibility, stability and trim.

Stolt Groenland's ship operator was aware of the potential for styrene monomer to polymerise and understood that the chemical should not be stowed adjacent to a heated tank. The ship operator assessed that the stowage of styrene monomer in 9S and the stowage of heated cargoes in 9P and 7S (i.e. separated by 9C and 8S) was acceptable.

[3] Ship voyage management software.

1.13 ONBOARD CARGO PROCEDURES

1.13.1 Planning and stowage

Stolt Groenland's safety management system (SMS) included a cargo and ballast operations manual that provided guidance on the various phases of cargo operations. The standard operating procedures section of the manual included:

> *Ship Operator stowage proposals as described in Cargo Orders Communication procedure are presented as proposals and must be closely studied taking into consideration the port and load berth rotation, draft, list, trim, loading sequence, etc. While operations try to give the Master maximum flexibility in making alterations, the Master and Chief Officer will often find that because of heating requirements, coating compatibility, tank sizes, pumps and cargo specifications, last cargo and customer requirements, there is often a limited choice of stowage.*
>
> *…It is the ship's responsibility to make a detailed check of proper cargo stowage based on the proposal received from the Ship Operator. ..*
>
> *The final stow is always subject to the Master's approval.*

No issues with the stowage of the styrene monomer cargo carried on board *Stolt Groenland* were raised by the tanker's master or C/O.

1.13.2 Cargo monitoring

The cargo and ballast operations manual also included:

> *Care for the Customers cargo does not cease after loading, it continues throughout the voyage to the discharge port and during the discharge. Some cargoes may require additional attention and control during the voyage in respect to their single or combined concerns to: safety, quality, handling, cleaning, costumer's demand etc. Ongoing cargo care is the most important aspect of the chemical tanker trade and the Chief Officer has the primary responsibility for conducting and recording these tasks…*

Voyage instructions required that the temperatures of cargoes requiring heating or cooling be recorded in a cargo temperature log at least once a day and for the log to be available for scrutiny by the receivers of the cargo at discharge ports. The instructions also required the temperatures of non-heated and non-cooled cargoes to be monitored for signs of abnormal activity such as polymerisation. There was no specific requirement for the temperatures of non-heated and non-cooled cargoes to be recorded.

1.14 IBC CODE

SOLAS[4] Chapter VII and MARPOL[5] Annex II require chemical tankers built after 1 July 1986 to comply with the *International Code for the construction and equipment of ships carrying dangerous chemicals in bulk and index of dangerous chemicals*

[4] International Convention for the Safety of Life at Sea, 1974, as amended.

[5] International Convention for the Prevention of Pollution from Ships, 1973, as amended.

carried in bulk (IBC Code). In addition to prescribing design and construction standards, The IBC Code tabulates the minimum requirements for over 750 dangerous chemicals.

References in the IBC Code to cargo temperature, inhibited cargoes, and cargoes not to be exposed to excessive heat, include:

Chapter 7 – Cargo temperature control

7.1.5 Means shall be provided for measuring the cargo temperature.

7.1.5.4 When overheating or overcooling could result in a dangerous condition, an alarm system which monitors the cargo temperature shall be provided. (see also Operational Requirements in 16.6.)

Chapter 15 – Special requirements

15.13 Cargoes protected by additives

15.13.3 Care shall be taken to ensure that these cargoes are sufficiently protected to prevent deleterious chemical change at all times during the voyage. Ships carrying such cargoes shall be provided with a certificate of protection from the manufacturer, and kept during the voyage, specifying:

1. *the name and amount of additive present;*
2. *whether the additive is oxygen dependent;*
3. *date additive was put in the product and the duration of effectiveness;*
4. *any temperature limitations qualifying the additives effective lifetime; and*
5. *the action to be taken should the length of the voyage exceed the effective lifetime of the additives.*

Chapter 16 – Operational requirements

16.6 Cargoes not to be exposed to excessive heat

16.6.1 Where the possibility exists of a dangerous reaction of a cargo, such as polymerization, decomposition, thermal instability or evolution of gas, resulting from local overheating of the cargo in either the tank or associated pipelines, such cargo shall be loaded and carried adequately segregated from other products whose temperature is sufficiently high to initiate a reaction of cargo (see 7.1.5.4).

16.6.2 Heating coils in tanks carrying this product shall be blanked off or secured by equivalent means.

1.15 SHIPPING INDUSTRY GUIDANCE

1.15.1 Tanker Safety Guide

The Tanker Safety Guide (2014) (TSG), was published by the International Chamber of Shipping to promulgate good practice. With reference to styrene monomer, the guide stated that polymerisation was very often initiated by elevated temperatures, which could reduce the effectiveness of the inhibitor or reduce the inhibitor's effective life. It also stated:

> *These inhibitors are designed to be effective for a set period of time at a specified temperature. It is therefore essential that the timed effectiveness of the inhibitor is sufficient for the voyage and includes a good safety margin.*
>
> *Since elevated temperature can reduce the effectiveness of the inhibitor, or reduce its effective life, it is essential that heat sources are kept away from these cargoes and that the temperature is closely monitored on at least a daily basis, or more frequently if recommended by the cargo manufacturer.*
>
> *An increase in cargo temperature that is not related to ambient weather conditions or adjacent cargo temperatures may be an early indication that a polymerisation process has started. In such instances, the cargo manufacturers should be contacted immediately to advise appropriate counter measures which may include the addition of more inhibitor or the cooling of adjacent structures. Should the increase in temperature be rapid then the decision to jettison cargo may be the only option in order to avoid serious structural damage to the cargo tank and the ship.*

Regarding cargo stowage and handling, the TSG included:

- *That heated cargoes will be stowed so as to be compatible with cargoes in adjacent tanks;*
- *That heated cargoes will be stowed so as not to be adjacent to heat sensitive cargoes or when a heat source could lead to a dangerous reaction;*
- *Some cargoes require an inhibitor to ensure that they remain chemically stable during transit. Such cargoes should not be stowed adjacent to heated cargoes;*
- *Some cargoes are liable to self react under certain conditions…The temperature of cargoes that may self-react should be closely monitored. Unexpected changes are an early indicator of a possible self-reaction. Should the temperature rise be in excess of what is expected, taking into account the ambient conditions and the temperature of adjacent cargoes, then this should be treated as an emergency and handled accordingly…*

1.15.2 Chemical Distribution Institute Guidance

The *Chemical Tanker Operations for the STCW Advanced Training Course – A Practical Guide to Chemical Tanker Operations (2018)* was produced by the Chemical Distribution Institute (CDI) to provide an aide-mémoire for crews and a study guide for advanced training in chemical operations.

Regarding the polymerisation and inhibited cargoes, among other things, the guide stated:

> *Heat can initiate polymerization in reactive monomers, producing yet more heat in an exothermic reaction.*
>
> *Inhibited self reactive cargoes: should not be loaded adjacent to heated cargoes and heating systems will require isolating.*

1.16 STORAGE AND HANDLING GUIDANCE

1.16.1 *Styrene Monomer: Safe Handling Guide (2018)*

The Plastics Europe *Styrene Monomer: Safe Handling Guide (2018)*[6] (the Guide) was produced by the Styrene Producers Association, members of which included Ineos Styrolution Europe GmbH and Shell Chemicals Europe BV. Ineos Styrolution provided copies of the safe handling guide to all its customers. The Guide was not referenced in Stolt's VCR, nor was it passed to *Stolt Groenland*.

The Guide referred to transportation of styrene monomer by road, rail, barge and sea. It included:

> *Heated adjacent cargoes should be avoided, even if separated by cofferdams.*
>
> *Styrene should not be loaded into cargo tanks adjacent or corner-to-corner to a cargo having a temperature of 30°C (86°F) or higher even if separated by a cofferdam. Heating styrene to above this temperature will reduce shelf life and increase the risk of polymerisation in the cargo tank.*

For styrene storage ashore, Appendix 2 of the Guide included the following checks for polymerisation:

- *Polymer content (< 10 ppm, depending on product spec.)*
- *Temperature (<< 2-3°C/day). If the temperature rises 1°C/day, it is advised to be alert and keep monitoring the temperature actively. Re-circulation could stop the temperature rise. A 2-3°C/day temperature increase is a typical indication of the onset of a runaway polymerization. The temperature needs to be monitored continuously.*
- *TBC levels (target >10 ppm wt). At temperatures below 15°C in the tank/container, weekly sampling should be sufficient; above 25°C daily sampling is recommended. Normal TBC levels are between 10 and 15 ppm (for some applications higher concentrations are required). Below 10 ppm TBC polymer levels can slowly increase; below 4 ppm the TBC is not effective and accelerated polymerization will occur.*
- *Oxygen levels (3-8 volume % in the vapour phase).*

[6] Plastics Europe is a Pan-European trade association representing plastics manufacturers, of which the Styrene Producers Association was a sector group.

It explained that in certain circumstances it is possible for a runaway reaction to occur even if there is TBC and oxygen present in the styrene. These included: the presence of contaminants; the presence of rust in the tank; high (local) temperatures (>40°C); and non-homogeneous distribution of the TBC and oxygen in the tank contents.

The guide also explained that TBC is not active long enough at high temperatures, since the reaction rate and therefore the depletion rate becomes too high. It included indicative depletion rates for TBC at varying temperatures **(Table 4)**.

Temperature	Depletion Days/1ppm	TBC Content	TBC Content	Shelf Life
°C		[Initial ppm]	[end]	Assured days
25	11	15	10	55
30	7	15	10	35
40	1.5	15	10	7

Table 4: TBC depletion in styrene (if stored under air)

1.16.2 Safe handling sheets

In addition to the *Shell Chemicals Cargo Handling Sheet* for styrene monomer that was referenced in *Stolt Groenland*'s VCR (see Section 1.9.1), similar guidance was provided by other styrene producers. Requirements for TBC concentrations and styrene temperatures contained in these guides are summarised in **Table 5**.

Producer	Recommended TBC for storage	Storage or carriage temperature	Maximum temperature	Remarks
Americas Styrenics	10-15ppm	Ambient	None quoted	Cooling recommended for storage where temperatures exceed 24ºC. Vessels containing styrene should be protected from external sources of heat.
Shell Europe	10-20ppm	Ambient	30ºC	Not adjacent to heat. Adjacent maximum temp 35ºC.
Lyondellbasell	10-15ppm	Ambient	30ºC	Styrene monomer should not be stored adjacent to tanks or compartments that are heated.
Chevron Phillips	10ppm	24ºC	30ºC	Stowed with respect to compatibility, heat adjacency and other requirements.

Table 5: Comparison of manufacturers' requirements for styrene monomer

1.16.3 Safety data sheets

SDSs are issued by chemical manufacturers in a harmonised format to provide generic safety information on products. SDSs are not specific to marine transport.

The transport information provided in the SDS for styrene monomer (stabilised) issued by Ineos Styrolution did not include guidance regarding the bulk transport of the product by sea.

1.17 RECENT INSPECTIONS, AUDITS AND VETTING

On 22 May 2019, *Stolt Groenland* was audited by a Stolt superintendent. The internal audit report noted that the SMS was well implemented, the senior officers were diligent, and that the tanker was very well maintained. Two non-conformities and 11 observations were recorded. The non-conformities concerned the absence of records of atmospheric checks when tank cleaning, and the recording of working hours. The observations were related to minor errors and omissions in documentation.

On 6 July 2019, *Stolt Groenland* was inspected by a Port State Control officer in Long Beach, USA. No deficiencies were identified.

On 6 August 2019, *Stolt Groenland* was vetted by a CDI inspector in Point Comfort, USA. One of the questions included in the CDI questionnaire was:

> *Are officers aware of the documentation and handling requirements for cargoes and inhibitors, and if the cargo carried is required to be inhibited, is the required information available?*

No deficiencies were recorded, and the vetting report noted:

> *Due to the various annex II cargoes carried on the vessel, current and previous cargo operations plans were checked and found in compliance with IBC and company procedures.*

And

> *Observed the cargo handling and monitoring equipment on deck and in the CCR during cargo operations and found in good condition overall.*

1.18 YEOMPO QUAY

The port of Ulsan was administrated by the authority of the Ministry of Oceans and Fisheries. The berths were managed and operated by three different entities; the Ministry, Ulsan Port Authority and private companies. In the case of Yeompo Quay, berths 1 and 2 were operated and managed by Ulsan Port Authority while berth 3, where the accident occurred, was operated by the Ministry.

Several berths and jetties in Ulsan harbour were specified for handling dangerous cargoes, and they were listed in the Ministry's publication *Safety Navigation Guide for Oil Tankers (Ulsan Port)*. The guide did not list Yeompo Quay as an authorised berth for handling dangerous cargo.

Stolt Groenland's berth at Yeompo Quay had been arranged by the ship's local agent who was given permission by the port authority to use it for ship-to-ship transfer operations.

1.19 STYRENE MONOMER ACCIDENTS AND INCIDENTS

1.19.1 *Stolt Focus*

During the investigation into the causes and circumstances of the explosion on board *Stolt Groenland*, MAIB was made aware of a styrene monomer polymerisation incident that occurred on board *Stolt Focus* a couple of weeks earlier.

Styrene loading

Between 3 and 4 August 2019, the Cayman Islands registered chemical tanker, *Stolt Focus*, also operated by Stolt, loaded 4900t of styrene monomer into nine stainless steel cargo tanks at the LBC Terminal, Houston. The styrene was produced by Ineos Styrolutions and the product was loaded from ST B503. The temperature of the styrene monomer in the shore tank was 13.33°C and the TBC concentration was 11.7ppm. The observed temperatures the styrene shortly after it was loaded on board were between 16.6 and 21.5°C.

The certificate of inhibitor issued by the attending ACA surveyor stated that 14 US gallons of liquid TBC had been divided between the cargo tanks and that the target TBC concentration was 21ppm. The effective days (60 – 90) and inhibitor statement shown on the certificate were identical to the certificate issued to *Stolt Groenland* **(Figure 18)**. The certificate was signed by the surveyor and the tanker's C/O.

Passage

Stolt Focus departed Houston on 12 August 2019 and arrived in Kobe on 13 September. At about this time elevated temperatures were discovered in some of the tanks containing styrene monomer and actions were taken to cool the cargo and contain the situation. The incident was not reported to the Flag State at the time.

On 20 November 2019, Stolt informed the Cayman Islands Registry that *Stolt Focus* had experienced a problem with the styrene monomer cargo. An email to the Registry included:

> *Stolt Focus observed a steady rise in temperature of the Styrene Monomer onboard, all our efforts to stabilize temperature rise failed, after consultation with our chemists it was decided to mix the Styrene Monomer with sea water to stop the reaction which was successful. As a result, we now have 4 tanks with this mixture which is now unpumpable and therefore we need to reduce viscosity by diluting with Benzine.*
>
> *SOLAS is not so clear on dilution of cargo's and we would like your guidance to ensure we do correctly and meet all relevant regulations. Our initial plan was to carry out alongside in Malaysia which is now a no go as we are unable to get permission from Malaysian authorities.*

Stolt proposed to dilute the styrene monomer with Benzine in international waters. The intended ratio facilitated the addition and mixing of the 'short stop' inhibitor[7] phenothiazine (PTZ), which would stabilise the styrene to enable its incineration ashore.

The Cayman Islands Registry approved Stolt's proposal subject to several conditions concerning: risk assessments, the readiness and functioning of equipment, enhanced monitoring, and the notification of transfer and disposal intentions to coastal states.

Request for further information

Due to the co-incidence of the heating of styrene monomer cargoes on board *Stolt Focus* and *Stolt Groenland* (same supplier, same port of loading, same shore tank, similar timeframe, similar trading route), the MAIB requested Stolt to provide further information on the circumstances leading to the remedial action taken on board *Stolt Focus*. Stolt refused to do so, as it did not consider the heating and subsequent disposal of the styrene monomer cargo to be a marine accident or marine incident.

A note on an emergency response team log sheet recorded during the *Stolt Groenland* accident stated 'Same *LOADING TERMINAL as S/FOCUS*'.

1.19.2 Other maritime accidents

In December 2019, the MAIB issued an interim report on the explosion and fire on board *Stolt Groenland* in which ship owners, ship and terminal operators, and individuals were requested to forward information on accidents or 'near-misses' involving the carriage of styrene monomer on board ships.

Only one response was received. This concerned one of four tanks of styrene monomer loaded in Houston that was rejected after a high concentration of polymer was identified at the discharge port in China. The temperature of the styrene monomer reached 37°C but was cooled by running water on the deck. In addition, inhibitor was provided by the discharge terminal, and was added in the presence of a P & I surveyor. The polymerisation of the styrene was checked, and the cargo was eventually brought back within specification by a specialist chemical contractor.

It was suspected that the polymerisation was caused by oxygen depletion in the styrene monomer. The vent stack from the styrene tank was next to a vent stack from a Hexene cargo that was nitrogen padded. As the nitrogen in the Hexene tank had to be topped-up by bottle through the vent stack, it was possible that the crew used the styrene vent stack in error and inadvertently introduced nitrogen into the styrene tank.

Stolt did not report any previous accidents or incidents involving styrene monomer.

1.19.3 Shore-based accidents

In the absence of a global chemicals accident database, the accidents resulting from runaway polymerisation of styrene monomer shown in **Table 6**, have been collated from several sources.

[7] A 'short stop' is a free radical scavenger that can be added to a polymerising system to temporarily halt the polymerisation. When the short stop is consumed the polymerisation will continue.

Date	Location	Injuries	Fatalities
7 May 2020	Visakhapatnam, India	>300	11
30 June 2005	Mesa, USA	0	1
8 April 2004	Jiangsu, China	0	1
2 April 2003	Addyston, USA	0	1
27 March 2000	Pasadena, USA	71	1
6 October 1999	Chiayi, Taiwan	1	0
23 June 1999	Pasadena, USA	21	2
27 June 1998	Channahon, USA	1	0
24 December 1998	Kanagawa, Japan	0	0
21 January 1998	Kaohsiung, Taiwan	4	0
26 January 1996	Chiayi, Taiwan	1	0
5 July 1994	Kaohsiung, Taiwan	0	1

Table 6: Land-based runaway styrene monomer polymerisation accidents since 1990

The identified causes of the accidents varied, but insufficient temperature monitoring was a common contributor.

1.20 STYRENE SAMPLE AND OVERALL ANALYSIS RESULTS

The sample of residue **(Figure 8)** and the overalls **(Figure 9)** recovered from *Bow Dalian* during the onsite investigation (see Section 1.4) were sent to LPD Lab Services Limited (LPD) for analysis. The laboratory used Fourier Transform Infrared Spectrometry (FTIR)[8] and Pyrolysis gas chromatography–mass spectrometry (pyGC-MS)[9] analysis to try to identify potential indications of causative factors in the explosion.

The LPD report stated that the depletion of TBC is affected by heat, water and air, with heat being the most important. LPD explained that additional inhibitor should be added when inhibitor levels drop below 10 ppm, and that normal levels are 10-15 ppm, but some customers require up to 60 ppm.

The laboratory analysis report found that:

- *The plastic blob was confirmed as polystyrene or a polystyrene based material.*
- *There were some indications of the occurrence of dimers and other products of styrene, that would be indicative of an uncontrolled polymerisation process having occurred.*

[8] FTIR is a sensitive technique particularly for identifying organic chemicals in a whole range of situations including solid, liquid and gas samples. FTIR can also be used to characterise some inorganic compounds.

[9] pyGC-MS is a method of chemical analysis in which the sample is heated to decomposition to produce smaller molecules that are separated by gas chromatography and detected using mass spectrometry.

- *There is no TBC detectable in the polymer blob material. This is expected and is further indication of uncontrolled polymerisation as it is expected TBC is consumed prior to the 'runaway' polymerisation process.*

- *Styrene was identified on the overalls. This was observed in all areas but appeared more intense in areas of contamination.*

- *In high contamination areas (contaminated overalls) TBC was identified.*

- *If it is assumed that the styrene contamination of the overalls took place at the same time of the polymerization reaction and explosion was observed, then it can be stated that inhibitor was present, and detectable.*

- *Whilst quantification was not undertaken in this investigation, the amount of TBC in the overalls is likely to be significantly above the detection level of trace contaminants (typically between 1-10ppm). Therefore, it is unlikely that the absence of TBC was key in the explosion.*

LPD found no other clear indication of any initiator compounds associated with the chemical initiation of polymerisation. Based on the results of its analysis, LPD concluded that:

> *At this point in the investigation it is thought that rather than being associated with a lack of TBC, which was clearly present from being found on the overalls, the runaway styrene polymerisation reaction is likely to be associated with insufficient dissolved oxygen during storage, perhaps from poor venting or mixing. So, the TBC was unable to control the rate of polymerisation. The heat removal would then be the driving factor in the polymerisation reaction promoting reaction acceleration or thermal runaway.*

SECTION 2 – ANALYSIS

2.1 AIM

The purpose of the analysis is to determine the contributory causes and circumstances of the accident as a basis for making recommendations to prevent similar accidents occurring in the future.

2.2 EXPLOSION AND FIRE MECHANISMS

It was evident, from the exponential temperature gradient for 9S recorded on the VDR **(Figure 17)**, that the explosion and fire on board *Stolt Groenland* resulted from the runaway polymerisation of the styrene monomer cargo. The sudden release of large quantities of vapour from the 9S p/v valve **(Figure 3)**, the activation of the high-level and high-high-level alarms on the bridge front in quick succession, and the rapid increase in the pressure within 9S that was seen by the C/O and 3/O in the CCR, support this.

The runaway polymerisation resulted in the rapid volumetric expansion of the styrene monomer, which increased the pressure within 9S at a rate that exceeded the venting capacity of the tank's p/v valve. As a result, the tank ruptured through the main deck and the common bulkhead with the empty cargo tank 9C **(Figures 11** and **12)**.

The styrene monomer vapour ignited almost immediately following the rupture. As the temperature of the cargo in 9S was well below the auto-ignition point for styrene monomer when the explosion occurred, ignition of the vapour must have been caused by an external source such as sparks created by static electricity or metal to metal contact during tank rupture.

2.3 INITIATION OF POLYMERISATION

Styrene monomer polymerisation is initiated by heat, the lack of dissolved oxygen, the lack of an inhibitor, or contact with free-radical initiators such as peroxides. To mitigate against these potential initiators, the styrene monomer carried on board *Stolt Groenland* had been:

- Loaded under air, which significantly reduced the likelihood of oxygen depletion.

- Inhibited with a quantity of TBC that was intended to remain effective for a minimum of 60 days given the cargo volume and the ambient temperatures anticipated during the voyage.

- Stored in stainless steel tanks that had been wall wash tested and visually inspected, which reduced the risk of contamination.

- Sample tested on completion of loading **(Figure 19)** and found to be within specification with the peroxide concentration of 6ppm being well below the allowable maximum of 50ppm.

- Stowed in tanks that were not adjacent to tanks[10] that contained cargoes that were required to be heated, and for which the heating coils had been blanked.

However, despite these precautions, runaway polymerisation occurred.

The styrene monomer carried in 9S had been heated to levels well above the ambient temperatures experienced during the voyage. The VDR data **(Figure 17)** showed that the temperature of the styrene monomer stored in 9S exceeded 37°C during the 29-day period between 30 August and 28 September.

The styrene monomer loaded in Houston had been maintained at 13°C in a shore tank; by the end the loading process on 8 August, its temperature had increased by about 4°C. Given that the ambient temperature in Houston was about 30°C and cargoes loaded into the tanks adjacent to 9S all exceeded 30°C, it is likely that the temperature of the styrene monomer would have reached or been higher than the maximum temperature of 29.4°C (85°F) specified on the certificate of inhibitor **(Figure 18)** when the vessel departed Houston on 17 August, and therefore during the whole voyage.

Although unlikely to have been the single cause of the runaway polymerisation event, the elevated temperatures significantly increased the rate of TBC depletion and therefore the risk of polymerisation. It was therefore apparent that the elevated temperature of the cargo in 9S was the key factor in this accident.

2.4 HEAT TRANSFER

As the air and sea temperatures in the Houston area, and during the tanker's passage to and through the Panama Canal, were about 30°C, it was inevitable that the temperature of the styrene monomer and the other 'ambient' cargoes would rise accordingly. Any further increase of cargo temperatures required additional heating.

The only source for the heating of *Stolt Groenland*'s 'ambient' cargoes was the heated cargoes, particularly the HMD in 8P to 11P, which was 61°C when loaded. The VDR **(Figure 17)** showed that the HMD temperature was being maintained between 45°C and 55°C by the periodic use of the vessel's cargo heating system. It also showed that, due to the effects of heat transfer, the temperatures of the cargoes in the adjacent centre tanks (8C to 11C) had settled at between 40ºC to 44ºC, and the corresponding starboard side tanks (8S to 11S) between 36ºC and 38ºC. That the HMD was loaded at such a high temperature and later heated above its specified maximum carriage temperature of 50°C, might not have affected its quality, but it would have exacerbated the levels of heat transfer.

The rate and degree of the heat transfer from the HMD cargo to the styrene monomer in 9S would have been influenced by the relatively low specific heat capacity (SHC) of the adiponitrile in 9C and that of the styrene itself **(Table 7)**. SHC is the amount of heat energy required to raise the temperature of a substance per unit of mass. A substance with a low SHC will heat up (and cool down) more readily than a substance with a high SHC. In this case, the adiponitrile and styrene would have readily heated, and avenues for heat loss through adjacent tanks, the empty ballast tanks below, and the sun-exposed deck above were limited.

[10] It should be noted that, contrary to guidance contained in the Plastics Europe's *Styrene Monomer: Safe Handling Guide*, 6C (which contained styrene monomer) was corner to corner with 7S (which contained a heated cargo).

Material	Specific heat capacity (J/kgK)
Water	4200
Glycerol	2400
Acrylonitrile	2090
Styrene	**1730**
Sodium (liquid)	1230
Adiponitrile	1190
Copper	0.386

Table 7: The specific heat capacity of various materials at 20ºC

2.5 POLYMERISATION INHIBITOR MIXING

The TBC concentration was calculated and not measured. It was then poured into the open tanks and the styrene monomer loaded on top of it with no means of mechanical mixing. Poor distribution of the TBC and oxygen in the styrene monomer can lead to low concentrations at certain zones in the tank, which could lead to runaway zones in the bulk contents.

The methods of adding and mixing the inhibitor on board *Stolt Groenland* were rudimentary and relied heavily on vessel and cargo movement during the voyage. Although the styrene monomer was loaded and its inhibitor added 10 days before the vessel departed Houston, these were tried and tested industry practices and, given the levels of TBC found in 6P and 6C after the accident, it is less likely to have been a factor.

2.6 POLYMERISATION INHIBITOR DEPLETION

The target TBC concentration on loading was 17ppm. This was based on the amount of TBC required to ensure it remained effective for the duration of the voyage i.e. above 10ppm on arrival. The certificate of inhibitor issued on behalf of American Cargo Assurance indicated that the TBC should have remained effective for a period of 60 to 90 days at a recommended temperature range between 15.6ºC and 29.4ºC (60ºF and 85ºF). The duration between loading the styrene monomer on board *Stolt Groenland* in Houston and its planned discharge in An-Ping, Taiwan, was 56 days.

Using the indicative depletion rates provided by Plastics Europe in its *Styrene Monomer: Safe Handling Guide* **(Table 4)**:

- At a temperature of 25ºC, the TBC would have depleted at a rate of approximately 1ppm every 11 days. At that rate, it would have taken 77 days for TBC levels to drop from 17ppm to 10ppm **(Table 8)**.

- At a temperature of 30ºC, the TBC would have depleted at a rate of 1ppm every 7 days and therefore could have dropped to 10ppm within 49 days. This was less than the duration the cargo was planned to be carried on board.

- At 37ºC, the TBC depletion rate would have been significantly higher.

Ambient Temperature ºC	Depletion rate (Days/1ppm)	Effective TBC content (17ppm – 10ppm)	Assured number of effective days
25ºC	11	7	77
30°C	7	7	49
40ºC	1.5	7	10.5

Table 8: Calculated TBC depletion using figures provided in the Plastics Europe *Styrene Monomer: Safe Handling Guide (2018)*

Tests carried out on the samples taken from 6P and 6C after the accident found the TBC content in each tank to be 8ppm and 7ppm respectively. As the temperature of the styrene monomer in 9s was 5 to 6°C higher than that in 6P and 6C, the depletion rate of its TBC would have been significantly higher and therefore, its concentration level on arrival Ulsan much lower.

TBC inhibitor is ineffective below 4ppm and at 40°C this level could be reached within 21 days. The laboratory tests conducted by LPD (Section 1.20) identified traces of TBC on the overalls worn by a crewmember who was working on *Bow Dalian*'s deck when vapour from 9S cargo tank was venting from its p/v valve. This suggests that TBC was still present in the styrene monomer at the time of the explosion. However, given the prolonged elevated temperature of the cargo in 9S, it is highly likely that the TBC had become ineffective at some point during the voyage and probably before *Stolt Groenland* arrived at Ulsan.

The elevated temperature of the styrene monomer in 9S and the reduced level of TBC, would have increased the likelihood of dissolved oxygen depletion in the styrene monomer and, consequently, increased the rate of polymerisation. As polymerisation is an exothermic reaction, the styrene monomer temperature continued to rise, and on 27 September it reached 65°C **(Figure 20)**, the threshold for runaway polymerisation – the point at which the reaction could no longer be arrested.

2.7 CARGO STOWAGE

The IBC Code requires cargoes that present a risk of a dangerous reaction due to localised overheating heating, to be loaded and carried adequately segregated from other products whose temperature is sufficiently high to initiate a reaction of cargo. Reference to this requirement was made in *Stolt Groenland*'s VCR, which also emphasised that '*heated cargoes will be stowed so as not to be adjacent to heat sensitive cargoes or when a heat source could lead to a dangerous reaction'*. Shell's cargo handling sheet for styrene monomer stated that the maximum temperature of the cargo in adjacent tanks should not exceed 35°C. Similar guidance was provided by other industry bodies. The *Styrene Monomer: Safe Handling Guide* went further and stated that '*styrene should not be loaded into cargo tanks adjacent or corner-to-corner to a cargo having a temperature of 30°C (86°F) or higher even if separated by a cofferdam*'.

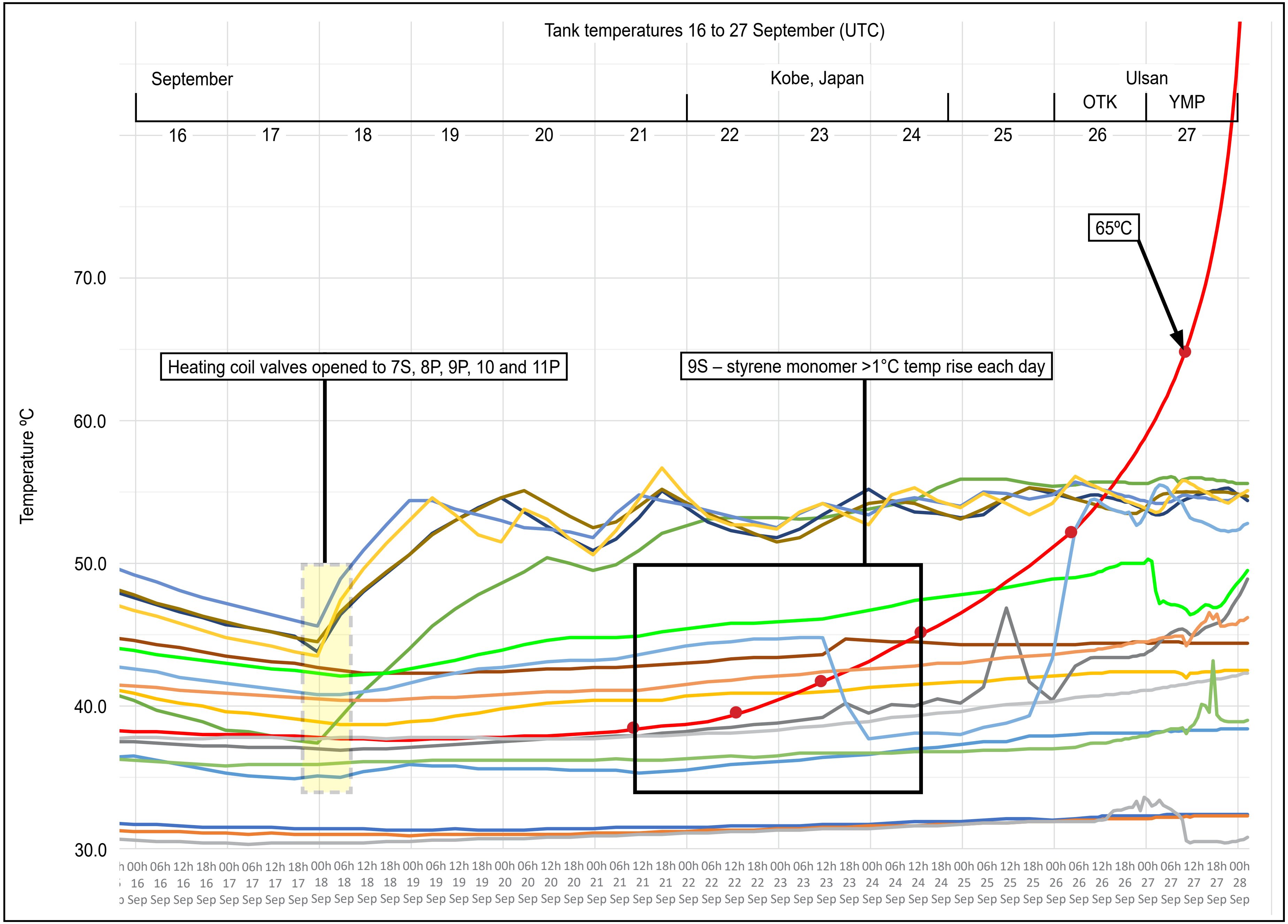

Figure 20: 9S Styrene Monomer Temperature 20-28 September

Some industry publications focussed on the need to physically segregate heated cargo from heat sensitive cargo rather than specifying maximum temperature limits for adjacent tanks. This approach did not take into consideration the risk of heat transfer from tank to tank across a cargo stow. The HMD in tanks 8P to 11P was clearly heated cargo and its temperature was maintained using the vessel's cargo heating system. The cargoes in tanks 8C to 11C were not considered to be heated cargo; however, because of heat transfer, they were being carried at temperatures well in excess of the limits set out by Shell and Plastics Europe. It was entirely foreseeable, and could not have been unexpected, that the styrene monomer cargo in 9S would be heated by the cargo in 9C, which itself been had been heated by the HMD in 9P. The likelihood of elevated temperatures due to heat transfer was acknowledged in the TSG, which stated that '*an increase in cargo temperature that is not related to ambient weather conditions or adjacent cargo temperatures may be an early indication that a polymerisation process has started*'.

The polymerisation of the styrene monomer on board *Stolt Groenland* indicates that the precaution of not stowing heat sensitive chemicals immediately next to heated cargoes is not always sufficient in meeting the 'adequate' segregation requirement of the IBC Code (see Section 1.14). The likelihood and extent of heat transfer from heated cargoes to heat sensitive cargoes via intermediate tanks must also be accurately determined.

The stowage of the styrene monomer on board *Stolt Groenland* was planned by an experienced ship operator using the iStow programme, and appeared to comply with the applicable regulatory and onboard requirements and to align with industry guidance. The tanker's C/O then scrutinised the proposed plan before it was approved by the master. However, although the maximum temperature of the styrene monomer cargoes, 85°F or 29.4°C, was stated on the certificate of inhibitor, no calculations were undertaken during the planning of the stowage to ensure that heating from adjacent tanks did not lead to this being exceeded. Instead, the ship operator, and the tanker's master and C/O relied on their experience. This stemmed from several factors, including:

- The calculation of heat transfer was complex due to the differing SHCs, tank construction, tank levels, stowage durations, and other variables. Consequently, it was outside usual practice.

- The complexity of the heat transfer calculation was such that it was outside the scope of the iStow software.

- The master and chief officer's knowledge of heat transfer was limited to the syllabus of the STCW training. They had also not previously encountered any difficulties when transporting styrene monomer.

The instructions and guidance that were available in the IBC Code, TSG and the CDI guide were clear that heat sensitive and heated cargoes should not be stowed in adjacent tanks. However, little or no emphasis was placed on industry guidance, the potential for heat transfer through intermediate tanks, or how such transfer was predicted. Instead, reliance was placed on temperature monitoring.

2.8 TEMPERATURE MONITORING

Stolt Groenland's SMS required the temperatures of all non-heated cargoes, which included the styrene monomer in 9S, and the adiponitrile in 9C, to be monitored daily. To assist in meeting these requirements and to comply with the IBC Code, remote temperature measurement and temperature alarms were available via the Ariston cargo monitoring system.

That *Stolt Groenland*'s crew were unaware of the elevated temperatures and polymerisation of the styrene monomer in 9S, until warned by the activation of the high-level alarm on the bridge front, indicates that the temperatures of the non-heated cargoes were not monitored at all, and that no temperature alarms were set. The crew also either did not notice, or did not recognise the significance of the elevated temperatures of the cargoes discharged in Kobe and Ulsan **(Table 2)**, notably 8C (43.6°C), 8S (39.1°C), 11C (48.2°C), 9C (48.8°C), 10C (46.0°C) and 11S (38.4°C). In Ulsan, such oversight might have been due to competing demands encountered by the off-going and incoming C/Os when handing over during cargo operations.

The absence of temperature monitoring of the non-heated cargoes stemmed from the crew's view that styrene monomer was a benign cargo when inhibited, and that no previous problems or difficulties with its carriage had been experienced. Consequently, whereas the temperature of the heated cargoes was monitored and maintained, primarily for reasons of quality, the styrene monomer and the other non-heated cargoes that were transported at 'ambient' were less of a concern, even if heat sensitive.

Had the temperatures of the styrene monomer been closely monitored and the maximum temperature of 85°F (29.4°C) stated on the certificate of inhibitor been adhered to, this accident would have been avoided. Concerns should have been raised and the charterer alerted well before *Stolt Groenland* entered the ports in Kobe and Ulsan, and maybe even before it left Houston. The charterer should have been informed once the temperature of the styrene monomer reached 30°C; this threshold was probably crossed before the vessel left Houston. The next opportunity to alert the charter and take urgent action was missed when the cargo temperature in 9S increased by 1°C on three consecutive days and 3°C in 24 hours **(Figure 20)**. These two events occurred on 24 September while the vessel was in Kobe and 4 days before the explosion. The runaway temperature of 65°C was reached at about 1000 on 27 September, shortly before *Stolt Groenland* moved to the Yeompo quay.

2.9 ACTION IN THE EVENT OF POLYMERISATION

The arrest of the polymerisation of styrene cargo in four of *Stolt Focus*'s cargo tanks was achieved ultimately by mixing the styrene with sea water (see Section 1.19.1). This action was successful, but it raises concerns over the options available to tanker crews encountering elevated styrene monomer temperatures.

The certificate of inhibitor for the styrene monomer issued to *Stolt Groenland* on completion of loading **(Figure 18)** stated that if the maximum temperatures were exceeded then the cargo should be monitored for the inhibitor level and polymerisation, and additional inhibitor added as required. However;

- *Stolt Goenland*'s crew had no means to test for TBC concentration.

- No means were available on board the tanker to test for polymers.

- The charterers did not provide additional TBC for the voyage.

- There were no means available to mix additional TBC with the styrene monomer.

As a result, even if *Stolt Groenland*'s crew had identified the elevated temperatures in 9S. 6P and 6C, the actions stated on the certificate of inhibitor were not viable.

In most cases, beyond monitoring tank and adjacent tank temperatures, and monitoring oxygen levels where a nitrogen blanket is used, the ability of tanker crews to prevent or arrest polymerisation of styrene monomer is limited to reducing tank temperatures either by cooling the tank exterior, or by flooding the tank with water. Therefore, it is important that the remedial actions to be taken, as listed on the certificate of inhibitor and associated guidance, are achievable and focused on sea transportation rather than shore-based processes. For reasons of expertise and practicability, this will probably be limited to seeking advice from cargo manufacturers or chemists ashore.

2.10 FIRE-FIGHTING

The immediate reactions of *Stolt Groenland*'s and *Bow Dalian*'s crews to supress the fire with fixed foam appliance, and to abandon their respective vessels, were positive and assisted in ensuring their own safety.

The fire on board *Stolt Groenland* burned for 5½ hours, during which time it spread from the manifold area to the accommodation block. The path of the fire spread was not clear during the on-site inspection, as the accommodation front was relatively free from significant damage. It is possible that the spread into the accommodation resulted from flammable styrene vapour entering from either the gas detection or cargo tank heating systems.

The actions of the local emergency services were also timely and considerable given that Yeompo Quay was a general cargo berth and, unlike chemical and oil product terminals, there were no enhanced fire-fighting arrangements or emergency response procedures in place. Given the berth's proximity to Ulsan and the Ulsan Bridge **(Figures 1** and **6)**, and the toxic smoke that was emitted from the explosion and fire, the potential consequences to the surrounding environment were severe.

2.11 *STOLT FOCUS* INCIDENT

The polymerisation incident that occurred on board *Stolt Focus* a couple of weeks earlier (Section 1.19.1) was of particular interest to the investigation as the two vessels had both loaded styrene monomer cargoes produced by the same supplier, in the same port, from the same shore tank during a similar timeframe. Furthermore, the voyage routes and therefore environmental conditions were similar.

A key difference was that the target concentration for the TBC on board *Stolt Focus* was significantly higher (21ppm rather than 17ppm). This might have been due to the planned carriage time, however, the calculated effective days documented on the certificate of inhibitor was the same for both vessels (60 – 90 days). The cargo stowage arrangements, the cause and magnitude of the elevated temperatures, and the circumstances that led to the elevated temperatures being identified on board *Stolt Focus* are unknown and therefore comparisons cannot be made.

It was disappointing that Stolt would not provide any details of the *Stolt Focus* incident, particularly as the company had apparently not experienced any other similar accidents or near misses while transporting styrene monomer. It was also surprising that the company did not consider the occurrence to be a marine incident[11] as defined in the IMO Casualty Investigation Code[12]. It is evident from the accident on board *Stolt Groenland* and the number of major styrene monomer explosions that have occurred on land, that the incident on board *Stolt Focus*, if not corrected would have endangered the safety of the ship, its occupants, and any other persons nearby. Therefore, in accordance with the Flag State regulations[13], it should have been reported.

In not reporting or informing other ships' masters of the *Stolt Focus* marine incident, an opportunity to avoid the explosion in Ulsan was lost. In not sharing the circumstances of the incident with this investigation, an opportunity for the wider industry to learn more lessons from the near miss has been lost. Regardless of any commercial sensitivities, it would be beneficial to future safety if Stolt would inform the chemical tanker industry of any additional lessons it has learnt from its styrene monomer polymerisation occurrences.

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[11] A marine incident means an event, or sequence of events, other than a marine casualty, which has occurred directly in connection with the operations of a ship that endangered, or, if not corrected, would endanger the safety of the ship, its occupants or any other person or the environment.

[12] Code of International Standards and Recommended Practices for a Safety Investigation into a Marine Casualty or Marine Incident.

[13] Cayman Islands' The Merchant Shipping Law (2016 Revision) – The Merchant Shipping (Marine Casualty Reporting and Investigation) Regulations, 2018.

SECTION 3 – CONCLUSIONS

3.1 SAFETY ISSUES DIRECTLY CONTRIBUTING TO THE ACCIDENT THAT HAVE BEEN ADDRESSED OR RESULTED IN RECOMMENDATIONS

1. The explosion and fire on board *Stolt Groenland* resulted from the runaway polymerisation of the styrene monomer cargo in cargo tank 9S. [2.2]

2. The polymerisation of the styrene monomer in 9S was initiated by the cargo's elevated temperature for much of the voyage, which reduced the effectiveness of the TBC inhibitor. [2.3, 2.6]

3. The elevated temperature of the styrene monomer in 9S resulted from the transfer of heat from the HMD cargo in the port side tanks, via the adiponitrile cargo in 9C. [2.4]

4. The precaution of not stowing the styrene monomer next to the heated HMD cargo was not sufficient in meeting the adequate segregation requirement of the IBC Code. [2.7]

5. The probability of heat being transferred from the HMD cargo tanks to the styrene monomer cargo was not fully considered during the planning and approval of the cargo stowage. [2.7]

6. Calculations to predict heat transfer during cargo stowage planning were not conducted because they were complex and outside the capabilities of the ship operator and the tanker's crew. They were also outside the scope of the cargo stowage software. [2.7]

7. Instructions and guidance were clear that inhibited cargoes should not be stowed adjacent to heated cargoes, but the likelihood of heat transfer through adjacent or intermediate cargo tanks was not covered in detail. [2.7]

8. Despite being a requirement in *Stolt Groenland*'s SMS, the temperature of the styrene monomer was not monitored, and the temperature alarms available on the cargo monitoring system were not set. The crew also either did not notice, or did not recognise the significance of, the elevated temperatures of the cargoes discharged in Kobe and Ulsan. [2.8]

9. The absence of temperature monitoring of the styrene monomer was influenced by the crew's view that it was a benign cargo when inhibited, and that no previous problems or difficulties with its carriage had been experienced. [2.8]

3.2 SAFETY ISSUES NOT DIRECTLY CONTRIBUTING TO THE ACCIDENT THAT HAVE BEEN ADDRESSED OR RESULTED IN RECOMMENDATIONS

1. The actions to be taken on encountering elevated temperatures in the styrene monomer cargo on board *Stolt Groenland*, which were stated on the certificate of inhibitor, were not viable. The crew had no means of testing for TBC concentration or polymers, and no additional TBC was carried. [2.9]

2. Given the proximity of Yeomp Quay to Ulsan and the Ulsan Bridge, and the toxic smoke that was emitted from the explosion and fire on board, the potential consequences to the surrounding environment were severe. [2.10]

3.3 OTHER SAFETY ISSUES NOT DIRECTLY CONTRIBUTING TO THE ACCIDENT

1. In not reporting or alerting other tanker masters to a similar polymerisation incident that occurred 2 weeks earlier, an opportunity was lost to prevent this accident. [2.11]

SECTION 4 – ACTION TAKEN

4.1 MAIB ACTIONS

The MAIB has issued an interim report that alerted the chemical tanker industry to the circumstances of the accident and requested information about previous similar accidents or incidents.

4.2 ACTIONS TAKEN BY OTHER ORGANISATIONS

Stolt Tankers B.V. has:

- Issued fleet notices highlighting issues with inhibited cargo carriage.
- Introduced a requirement for ships to report cargo temperatures to the ship operator ashore three times per week.
- Revised procedures for the setting of cargo-related alarms.
- Enhanced procedures for the checking of cargo stowages that contain both heated and inhibited cargoes.
- Commenced a concerted campaign through its marine compliance officers to raise crew awareness of inhibited cargoes.
- Started to investigate the possibility of upgrading its cargo stowage software to calculate and predict heat transfer within a stowage containing both heated and heat-sensitive cargoes.
- Started to work with manufacturers and industry bodies to ensure that cargo-handling instructions and protocols for inhibited cargoes are practical and achievable.
- Investigated the use of polymer testing equipment on board ships. Unfortunately it was not considered a viable prospect with current technology.

The Ministry of Oceans and Fisheries, Republic of Korea has prohibited ship-to-ship transfer operations for dangerous cargo on general cargo berths in Ulsan.

The International Chamber of Shipping has amended the Tanker Safety Guide (Chemicals), published January 2021, section 6.3.4 Stowage planning, to make it clear that:

- The stowage of heated and inhibited cargoes can result in a dynamic situation in which the degree of heat transfer may be complex and difficult to predict.
- One tank separation between heated and heat sensitive cargoes might not be sufficient.

The Chemical Distribution Institute has instigated the production of a best practice paper regarding the dosing of ship cargo tanks which will address, among other things, inhibitor quantity validation.

SECTION 5 – RECOMMENDATIONS

Cayman Island Shipping Registry, through the UK as the Member Government for the Red Ensign Group to the International Maritime Organization, is recommended to:

2021/117 Propose to the IMO a revision to Section 15.13 of the IBC Code to:

- Include in the certificate of protection the actions to be taken in the event of a cargo falling outside of the manufacturer's specified oxygen and temperature limits, and that

- Any actions should be realistic, taking account of the limitations on board ships regarding the monitoring, adding, and mixing of inhibitor during the voyage.

International Chamber of Shipping is recommended to:

2021/118 Promulgate this report to its members.

INTERTANKO is recommended to:

2021/119 Promulgate this report to its members.

Chemical Distribution Institute is recommended to:

2021/120 Amend its publication '*Chemical Tanker Operations for the STCW Advanced Training Course – A Practical Guide to Chemical Tanker Operations*' to make it clear that:

- The stowage of heated and inhibited cargoes can result in a dynamic situation in which the degree of heat transfer may be complex and difficult to predict.

- One tank separation between heated and heat sensitive cargoes might not be sufficient.

- Promulgate this report to its members.

Plastics Europe (Styrene Producers Association) is recommended to:

2021/121 Work with its members to incorporate the lessons learned from this accident in its *Styrene Monomer: Safe Handling Guide.*

Stolt Tankers B.V. is recommended to:

2021/122 Share with INTERTANKO the circumstances and lessons learned from the *Stolt Focus* incident and the results of its research into improved stowage software, to enable prediction of heat transfer and cargo behaviour.

Safety recommendations shall in no case create a presumption of blame or liability.

Marine Accident Report