CEDRE
EXPERTISES EN POLLUTIONS ACCIDENTELLES DES EAUX

Incident information sheet of IEVOLI SUN 2000

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The incident

On Monday, 30 October 2000 at 4h30, the CROSS Corsen received a distress call from the *Ievoli Sun*, a chemical tanker under Italian flag. The vessel, manned by 14 people, was in the middle of a storm, 45 Nautical miles off Batz Island. She left Fawley (united-Kingdom) and was on her way to Barcelona with a cargo of 6,000 tonnes of chemical products.

The captain signalled a water intake in its double-hull at the bow. The maritime prefect for the Atlantic sent out the *Abeille Flandre*, stationed in Ushant, to assist the vessel. A Super Frelon (helicopter) and an assessment team were mobilised. On site at 8h05, they witnessed the poor state of the vessel and airlifted the crew. The operations were successfully over at 9h20. At midday, the maritime prefect activated the Polmar-Sea plan.

The *Abeille Flandre* arrived on site. Due to the metocean conditions, the risk of grounding and major pollution on the coastline of Côtes d'Armor quickly became evident. After analysing the possible options, a team was deployed on the vessel from the air and attached a tow cable to the *Abeille Flandre*. The towing operations started at 17h15, with a speed of 4 knots due North-East, which was the only possible trajectory due to the weather and the state of the vessel.

On 31 October at 9h00, two thirds of the way towards the refuge in Cotentin, the *Ievoli Sun* sank 9 Nautical miles North of the Casquets (12 off Aurigny and 20 off the Hague) down 70 m.

Circumstances

In a couple of hours, the management of the situation was transferred. The maritime prefect for the Channel and the North Sea was in charge of operations on the French side. He knew since 30 October, that the vessel carried 160 tonnes of fuel oil and 40 tonnes of diesel in bunker, added to a cargo of 3,998 tonnes of styrene, 1,027 tonnes of Methyl Ethyl Ketone (MEK) and 996 tonnes of Isopropyl alcohol (IPA).

Styrene	
Quantity (tonnes)	3,998
Owner	Shell, Netherlands
Origin	Rotterdam, Netherlands
Destination	Berre, France
Methyl Ethyl Ketone (MEK)	
Quantity (tonnes)	1,027
Owner	Exxon, United-Kingdom
Origin	Fawley, United-Kingdom
Destination	Genoa, Italy

Isopropyl alcohol (IPA)	
Quantity (tonnes)	996
Owner	Esso Chemical, Belgium
Origin	Rotterdam, Netherlands
Destination	Barcelona,Spain

Due to the potential risk for pollution in the air created by the presence of styrene in the cargo and pollution in water due to the propulsion fuel, aerial and nautical monitoring missions were immediately carried out using French and British vessels. Maritime freight routes were deviated. First observations only showed a few slicks.

Work organisation

The vessel sank in international waters, at the limit between French, British and Channel Islands waters. Directly after, as part of the Channel Plan, the English authorities sent multiple representatives of the Maritime Coastal Agency (MCA) in Cherbourg, where the maritime prefect had established the Polmar command post. The prefect for the Channel activated the Polmar-Land Plan on Tuesday, 31 October at 19h00. He set up the first Polmar command port for all services in the prefecture of Saint-Lô.

On 1 November, the western defense zone, coordination for the Polmar-Land, opened a *Ievoli Sun* crisis cell in its area command post of Rennes, which was still operational after the *Erika* incident.

The General Secretary for the Sea piloted in-depth discussions between national experts and experts from the charterer regarding technical solutions for risk management related to the wreck. The charterer and its P&I Club signed a contract with Smit Tak Co, after validation from British and French authorities, on 10 April 2001. The object of the contract was the intervention on the cargo of the *Ievoli Sun* through a controlled release at sea of the MEK, IPA and diesel, followed by pumping operations of the styrene and heavy fuel oil. Treatment ended for the wreck on 31 May 2001.

During this incident, the international cooperation was quick and effective. The Channel Plan was implemented with Great-Britain, which was involved in all steps of the operation. The *Neuwerk*, a specialised German vessel, was mobilised as part of the Bonn Agreement. Continuous data sharing was carried out with the European Commission. 7 experts sent by the Italian government came to support their French counterparts as part of the European Task Force.

A year after the *Erika*, the incident of the *Ievoli Sun* was a reminder that oil pollution from oil tankers are not the only dangers for the coastlines.
Regarding human safety and pollution in the marine environment, chemical tankers could be a major issue due to the products they transport, without forgetting their propulsion fuel.

Moreover, this incident showed once more the knowledge limits regarding:

- the behaviours of chemicals spilled in sea water or stuck in tanks inside a sunken wreck;
- their potential impact on marine flora and fauna.

Once again, environmental and economic aspects are to be taken into consideration.

The levoli Sun sinking

Knowledge of the product: Methyl Ethyl Ketone (MEK)

1 – Characteristics

Synonyms: MEETCO, butanone, 2-butanone, butane-2-one, methyl acetone, methylpropanone

- formula: C4H8O or CH3COC2H5 molecular mass: 72.10 MARPOL class: III
- danger code n° UN: 1193 CAS n°: 78-93-3 IMDG class: 3.2 danger class: 33
- aspect, state at ambient temperature (20°C): colourless liquid, smell similar to acetone (DMK)
- relative density to water: 0.81 relative density to air: (vapour) 2.4
- fusion point: -86°C boiling point: +79,6°C
- flash point: -6 to -1°C vapour pressure: 77.5 mm Hg (20°C)
- solubility in water: 353 g/L (at 10°C) / 263 g/L (at 20°C)
- % vaporisation / % dissolution: 44% / 56%

2 – Physico-chemical behaviour of the product

Stability: stable.

- In the air: highly volatile, explosive mixture with air (LIE: 1.8 – LES: 11.5 % vol.), vapours heavier than air. Self-combustion at 505-515°C.
- in water: no reaction but highly soluble.
- reactivity with other products: may react with oxidising products, violent reaction with oleum, chlorosulfuric, sulfuric and nitric acids, aliphatic amines…

3 – Response techniques in the event of a spill

Emergency measures:

- isolate: 50 m around the site
- stay upwind
- avoid low points and air out an enclosed area before entering
- eliminate all combustion source, if possible: stop the leak.
- prevent infiltration in sewer systems, underground, in enclosed areas, the water basins of a port… using bunds or soil/sand dams.
- avoid touching the product or breath it in (stay upwind)

Possibility to transfer: explosion-proof pumps, plastic storage tanks (polyethylène, polypropylene, butyle).
- spill on land or on a quay: evacuate and area of 300 m downwind, confine then recover or let vaporise depending on the volume and doability.
- spill in water: contain the spread of the product using floating booms, skimmers if the slick is thicker than 1 mm, otherwise, let the product vaporise while monitoring eventual combustion source.

4 – Risks for the operators

- interventional limit: major risk = extreme combustion and explosion risk when mixed with the air, spread of heavy vapours close to the ground or water surface (after a quick spread in sewer systems, basins, ports…).
- poisoning risk: exposition limit for an hour of 100 ppm in the air (290 mg/m^3). Alert through the noticeable nice smell from 2 ppm or 6 mg/m^3 (depending on smelling ability from 1 to 150 mg/m^3).
- direct involuntary contact of the skin with the liquid is not dangerous (temporary discolouration after 5 min. of contact).
- choice in the protective equipment: yes, autonomous breathing apparatus, complete hazmat suit, rubber gloves and boots.

5 – Risks for the Environment

- immediate effects: low toxicity on fish populations (LC50 = 1.3 at 8.9 g/L) with risk of release of organohalogen compounds more toxic than the initial MEK, provided that the environment contains free halogens.
- persistence: quick photochemical disintegration in the air. In the ground or in a water environment, no bioaccumulation (quick biodegradation: 20 mg/L dissipates in 2-3 days in an airtight water environment).

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Knowledge of the product: Isopropyl alcohol or IPA

1 – Characteristics

Synonyms: IPA, Isopropyl alcohol, secondary propylic alcohol, Isopropanol, 2-Hydroxypropane, 2-Propanol, Dimethyl carbinol, Propanol, Hartono, Propel – formula: C3H8O or (CH3) 2-CH-OH molecular mass: 60.10 MARPOL class: III

- danger code n° UN: 1219 CAS n°: 67-63.0 IMDG class: 3.2 danger class: 33
- aspect, state at ambient temperature (20°C): colourless mobile liquid, smell of alcohol
- relative density to water: 0.785 at 20°C relative density to air: 2.67
- fusion point: -86 to 89°C boiling point: +82,4°C
- flash point: +12°C vapour pressure: 32 mm Hg at 20°C (57 mm Hg at 30°C) in water: soluble in any proportion and miscible in alcohol, acetone…
- % vaporisation / % dissolution: 19 % / 81 % viscosity: 78- 79 cSt at 20°C, 85 cSt at 25°C

2 – Physico-chemical behaviour of the product

Stability: stable.

- in the air: highly flammable and airborne especially in the event of spills on land (combustion point 400°C); explosive for temperatures > 12°C explosion limits = 2.3 to 12.7 % vol.
- in water: floats and mixes (complete dissolution with heat radiation); depending on the temperature and wind, light vaporisation; not corrosive.

reactivity with other products: violent reaction with powerful oxidising products, hot aluminium, sulphuric and nitric acids, aliphatic amines, strong bases, isocyanates…

3 – Response techniques in the event of a spill

Emergency measures:

- isolate 50 m around the site
- stay upwind
- Avoid low points
- air out an enclosed area before entering
- eliminate all combustion source, if possible: stop the leak.
- prevent infiltration in sewer systems (clog drains), , in enclosed areas (explosion risk), the water basins of a port (using bunds or soil/sand dams).
- avoid touching the product or breath it in (stay upwind).

Possibility to transfer: explosion-proof pumps, plastic storage tanks (polyethylène, polypropylene, butyle).
spill on land or on a quay: evacuate a 300 m area downwind, drain and contain to recover or absorb on a low point. Once a worksite is completed, clean with water or

let residual pollution vaporise.
spill in water: if the pollution has not been stopped before reaching the water, containment is impossible (complete quick dissolution). Let alcohol spread and vaporise while monitoring potential combustion sources.

4 – Risks for the operators

- interventional limit: major risk = combustion and explosion risk when mixed with the air, spread of heavy vapours close to the ground or water surface (after a quick spread in sewer systems, basins, ports…).

- poisoning risk: low toxicity, the exposition risk is of 400 ppm (980 mg/m^3) on the short-term: 15 mn (IDLH) and 3,100 ppm for an exposure of 8 hours (TLV). Danger warning by smell between 40 and 100 ppm. Risk of nausea, vomiting, and narcotic effect at high dosage > 500 ppm.

- choice of protection equipment: control with explosimeter. Protection equipment depending on the needs. In an enclosed area or on the long-term: protection or airways.

5 – Risks for the Environment

immediate effects: medium toxicity in water on fishes (LC50 from 900 to 1,100 mg/L in 24 h).

persistence: no bioaccumulation. relatively quick biodegradation in water (half-life of a couple of days).

Knowledge of the product: Styrene

1 – Characteristics

Synonyms: monomere styrene, ethenylbenzene, Phenylethylene, Styrol, Vinylbenzene – formula: C6H5-CH= CH2 molecular mass: 104.14 MARPOL class: B

- danger code n°UN: 2055 CAS n°: 100-42-5 IMDG class: 3.3

- aspect, state at ambient temperature (20°C): colourless to light yellow

- relative density to water: 0.906 relative density to air: 3.6

- fusion point: -30.6°C boiling point: 145.2°C

- flash point: 31°C vapour pressure: 670 Pa at 20°C

- solubility in water: 40 mg in 1 L of distilled water at 13°C, 20 mg in 1 L in salt water at 13°C (CEDRE data) – IDHL / TWA: 700 ppm / 50 ppm
- viscosity: 0.7 mpa.s at 25°C

2 – Physico-chemical behaviour of the product

stability: stability is assured by adding polymerisation inhibitors (example: 4-tert-Butylcatechol) at a rate of 10 to 15 ppm.

In the air: highly volatile, explosive mixture with air (LIE: 1.1 % – LSE: 6.1 % vol.) self-combustion temperature: 490°C, vapours heavier than air with a smelling threshold of 0.1 ppm.

In water: insoluble but able to polymerise under sunlight.

reactivity with other products: can violently react with strong oxidising agents such as peroxydes, as well as with bases, acids, and halogenures.

3 – Response techniques in the event of a spill

Emergency measures:

- contain populations in an area of 500 m around the slick
- in the event of a fire, the styrene may massively explode: evacuate in an area of 1 km (distance depends on the amounts)
- stay upwind
- Avoid low points
- air out an enclosed area before entering.
- avoid introduction in sewer-systems (clog the drains) and enclosed areas (explosion risk).

spill on land or on a quay: evacuate a 500 m area downwind, drain and contain to recover or absorb on a low point. Avoid pollution of the water in the port area by deploying bunds or soil/sand dams.
spill inn water: if possible, prevent the slick from reaching riverbanks or the shoreline using floating booms, then consider containment followed by recovery or absorption.

4 – Risks for the operators

Intervention limits: major risk = explosive combustion, propagation of vapours which make interventions on water difficult.
poisoning risk: product classed as irritating for the eye; inhalation above a certain limit can lead to chemical pneumonia. Repeated exposure can lead to liver lesions and damage to the nervous system.
measuring devices: control with an explosimeter, a PID sensor (equipped with a lamp adapted for styrene) as well as Draeger tubes:

- Monostyrolene 10/a n°6723301 from 10 to 200 ppm;
- Monostyrolene 10/ b n°6733141 from 10 to 250 ppm;
- Monostyrolene 10/ c n°CH27601 from 50 to 400 ppm.

choice of protective equipment: wear a type 3 hazmat suit and a complete breathing apparatus (eyes, mouth, chin) equipped with a gas and organic matter filter (type A2). polyethylene EVA laminated gloves.
Warning: butylic rubber, neoprene and polyvinyl chloride have a protection time below an hour.

5 – Risks for the Environment

immediate effects: product considered as toxic (acute toxicity from 1 to 10 mg/L) and the predicable concentration without effects is of 41 micro-g/L. In sea water, toxicity varies between 2 and 100 mg/L depending on the organisms.

persistence: low bioaccumulation, persistence estimated to 1 week.

Observations and measures

Expert committees

At the beginning of November, the expert committees mobilised by the MATE (French Ministry for the Land and Environment) and, in Rennes, by the deputy prefect for the Western defense area, detailed the risk characteristics of styrene and the measures to implement to guarantee the protection of operators and, if needed, of coastal populations (in the event of inhalation of styrene vapours or sea products consumption following styrene sorption).

Initiated by the national experts committee implemented by the Ministry for Regional Planning and the Environment, multiple experiments were carried out in CEDRE's infrastructure to study the behaviour of styrene on the surface of water, the risks of polymerisation in the vessel and the contamination, in the event of a spill, of seafood (crabs, mussels, and oysters) with analyses by the municipal laboratory in Rouen and smell tests by the ISPN (Nuclear Safety and Radiation Protection Authority).

Observations and measures

At sea, aside from the operations for the management and safety of users, the French Navy coordinated, in close cooperation with British authorities and resources, operations for the detection and measurement of pollutants. Regular monitoring around the wreck using aircrafts (planes and helicopters) from the French Navy, Customs and British coastguards, to detect potential pollutions on the surface.

Using these resources and those of the maritime affairs, sampling of air and water were regularly carried-out for the experts committee of the western defense area. Most samples were taken and analysed by the LASEM (the Analysis, monitoring and expertise laboratory for the French Navy) in Cherbourg. During the first weeks, on land and in Aurigny, the marine firefighters of Marseille, accompanied by a Civil Security Instruction and Intervention Unit, were placed under the authority of the prefect for

the Channel. Their mission was to create a network for the detection of styrene vapours in the air, which always revealed negative measures.

Ifremer also created a monitoring network for the quality of the marine environment to analyse water and living matter.

Characteristics and general behaviour of the three chemicals

Methyl Ethyl Ketone (MEK)

Methyl Ethyl Ketone (MEK) is used to synthesise solvents (paint, glue), as extraction solvent (papers, dewaxing of oils) and for organic synthesis. It is a stable product, highly volatile and explosive when mixed with water. The vapours, heavier than air, and its nice smell, are noticeable at a concentration of 2 ppm. According to the MARPOL classification, this product is classified as class III, as IPA.

Methyl Ethyl Ketone (MEK)

Formula	CH3 CO C2H5
Danger code	UN n°: 1193 – IMDG class: 3.2
Aspect at 20 %	Colourless liquid, acetone smell
Relative density	Water: 0.81 – Air: 4.4
Flash Point	-6 to -4°C
Solubility	Highly soluble in water: 353 g/l at 0°C

Isopropyl alcohol (IPA)

Isopropyl alcohol is used in the synthesis of solvents (paint, polish) extraction of essential oils, purification of pharmaceutical products, sugar/starch/platinum dehydration, in organic synthesis and in antifreeze. It is a stable product, highly flammable and highly volatile. It floats and mixes with water. It is MARPOL Class III: practically non-toxic substance for aquatic life, no bioaccumulation in the soil or in aqueous environments. IPA therefore presents very low toxicity risks for human health and the environment. The risk is more important regarding combustion or explosion in the event of massive release in the air.

Formula	(CH3)2 - CH - OH
Danger code	UN n°: 1219 – IMDG class: 3.2
Aspect at 20 %	Mobile colourless liquid

Relative density	Water: 0.785 – Air: 2.67
Flash Point	+ 12°C
Solubility	Soluble in all water rates

Isopropyl alcohol (IPA)

Styrene

Styrene is a basic component used in the manufacturing of polymers and copolymers (polystyrene, ABS-Acrylonitrile butadiene styrene, synthetic rubber, resins, polyester, styrene alkyls, ion exchanging resins) and in organic synthesis. This product is highly volatile and explosive when mixed with water. During transportation, stability is assured by adding polymerisation inhibitors. Its vapours, heavier than air, are classified as irritating for eyes and airways. The olfactory threshold is of 0.4 ppm. This is a class B product in the MARPOL classification (created by the IMO – International Maritime Organisation). Class B products are substances which have a persistence of one week or less after bioaccumulation, or substances that might alter seafood products, or substances which are toxic for aquatic life. In sea water, toxicity thresholds vary between 2 and 100 mg/L depending on the organisms. The risk would essentially concern the plume created by product vaporisation in the event of massive releases.

Styrene, monomere styrene	
Formula	C6H5 - CH = CH2
Danger code	UN n°: 2055 – IMDG class: 3.3
Aspect at 20 %	Colourless to light yellow liquid
Relative density	Water: 0.906 – Air: 3.6
Flash Point	+ 31°C
Solubility	280 mg/l at 20°C

Behaviour of MEK and IPA studied by CEDRE

To evaluate the behaviour of MEK and IPA in the event of controlled releases, the dissolution kinetics of these products were studied by CEDRE in an artificial water column, specifically created for this purpose, of 3.5 m in height to 16 cm in diameter, filled with seawater. The products were injected using a pump a variable depths and rates. To visualise the behaviours of these products, a dye (organol red) was added to them.

For MEK:

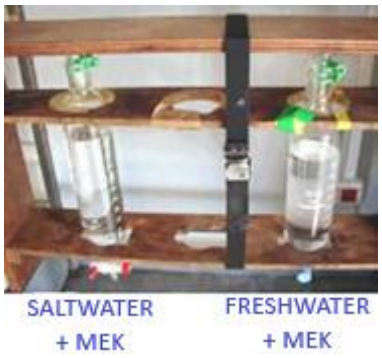
Solubility measure

- In sea water:

Tests were carried out, in CEDRE's infrastructure, at the request of the *levoli Sun* national experts committee regarding the solubility of MEK in sea water. A solubility rate of 158 g/L at 25°C was measured.

- In fresh water:

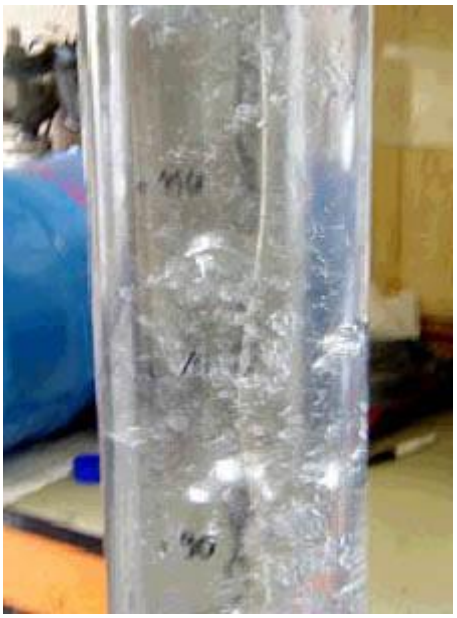
A solubility rate of 223 g/L at 25°C was measured.



Measure of solubility in sea water and fresh water ©CEDRE

Behaviour of MEK

Despite the high solubility rate of MEK in sea water (158 g/L at 25°C), almost all of the product reaches the surface in the event of an uncontrolled sudden release, as the refloating time is too short for good dissolution.
However, if the flow is restricted, with the creation of bubbles of MEK, these bubbles do not reach the surface as MEK dissolves during refloating.



Methyl Ethyl Ketone ©CEDRE

Methyl Ethyl Ketone (MEK) + dye ©CEDRE

MEK was classified as a soluble product but the results obtained showed that release must be carried out at a low rate. Indeed, it was not possible to exclude the creation of a slick on the surface, with an eventual impact on the environment and the operators.

IPA:

the tests carried out showed that IPA is a product which directly dissolves in sea water without presenting any particular risk.

Behaviour of styrene studied by CEDRE

Solubilisation

To better manage solubility in laboratories, which only took into account, depending on the documentation, dissolution in fresh water. Comparative tests were therefore carried out by CEDRE using sea water and distilled water.
Analyses showed a solubilisation rate of styrene twice more important in fresh water than in sea water (40 mg/L against 20 mg/L during tests) which led to the reconsideration of the reference value of 200 mg/L.

Vaporisation

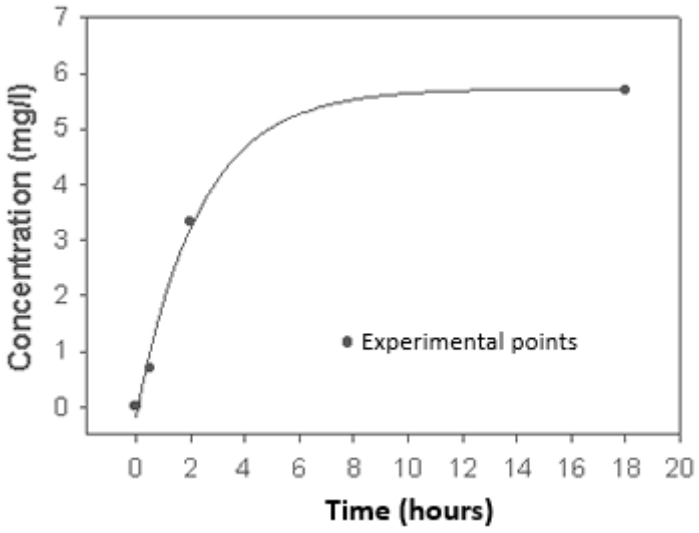
Field experiments were carried out to understand the behaviour of styrene after a spill on the surface of the sea (release of 10 litres of styrene on a surface of 10 m² with agitation).
Vaporisation and dissolution kinetics was studied in detail, as well as the potential for polymerisation.

Release of styrene ©CEDRE

Regarding vaporisation processes, explosivity measures remained below the detection thresholds of CEDRE's sensors (two explosimeters from different brands). Analyses carried out on gas emissions by Brest's marine firefighters did not reveal significant presence of styrene in a gas state (use of Dräger tubes). However, a strong styrene smell was noticed coming from the test tank.

Dissolution

Samples taken to evaluate the dissolution processes helped reveal the evolution of styrene crates in the water column. This rate was at its peak after 18 hours. There was no styrene remaining on the surface of water at the end of the test and therefore no more dissolution possibility.
The maximal value of 6 mg/L is largely inferior to reference values noted in previous documentation (of about 200 mg/L).
The repartition of styrene at the end of the experiment was as follows: 99.4 % in the air and 0.6 % in the water column.



Assessment of dissolution processes of styrene in water ©CEDRE

Polymerisation

The ability to polymerise styrene in marine conditions was studied by CEDRE. After 2 hours of contact, it seems that styrene could create micro-emulsions. The aspect of the product in this new form was close to the one of a polymer but analyses showed that it was still the initial monomere styrene.

In test conditions which were as close to real conditions as possible, the main behaviour of the product was vaporisation. The dissolution process was very limited (maximal value of 6 mg/L) and largely inferior to the one available in previous documentation (dissolution up to 200 mg/L).

Measure of explosivity ©CEDRE

No explosive risk was noted and the values in the air never exceeded 10 ppm. However, the scale difference with a massive spill at sea did not allow to presume the rates which could be reached in a real environment. Finally, no polymerisation was detected; the formation of micro-emulsions under the effect of waves could explain particular colourations of styrene and lead to think that it was a different product.

Product after release ©CEDRE

Water sampling ©CEDRE

What was described here is was only valid in the experimental conditions and for its duration. These results should only be considered for indication. The product could behave slightly differently after being put under pressure, possibly in partial contact with water, then refloated and put under real maritime conditions. Sampling on site would be essential to remove any doubt.

In complement to these field experiments, laboratory analyses were carried out to confirm the composition of styrene, which were communicated by SHELL and showed a 99.9 % purity rate with:

- 12.7 mg/kg of stabilising products (PTBC);
- 0.9 mg/kg of polystyrene;
- 36 mg/kg of aldehyde;
- 3 mg/kg of peroxide;
- less than 0.2 mg/kg of chlorine;
- less than 0.2 mg/kg of sulphur;
- 75 mg/kg of water.

The communication from SHELL, dated from 1 November 2000, precised that all elements were typical according to ASTM norms.

Complementary data on styrene: according to the British centre CEFAS https://www.cefas.co.uk/ (Centre for Environment, Fisheries and Aquaculture Science), styrene should not polymerise in less than:

- 170 days at 15.6°C
- 1 year at 4-5°C

These elements give a delay of 7 months at least before polymerisation, in the expected temperature conditions of the area.

Test results for the study of polymerisation in marine conditions, in a test tank and in a laboratory setting.

Protocol

Test tank:

Stainless steel tanks of 160 and 200 litres were kept submerged in on of CEDRE's sea water test tanks to not potential polymerisation signs using:

- stabilised styrene in an airtight tank (Pf),
- stabilised styrene in a slightly open tank with access to basin water through a small bunghole (Po),
- Stabilised styrene in a completely open tank (Go),
- non-stabilised styrene in a completely open tank with access to basin water (Go ns).

The tanks were submerged on Friday, 22 December 2000. Analyses were carried out following protocols given by Shell Chemistry.

In CEDRE's laboratory:

A small-scale test was carried out in a laboratory, at 30°C, in two stainless steel beakers:

- One with stabilised styrene and water flow,
- the other with stabilised styrene and no water flow.

Results

Test tank:

In the test tank, only the styrene without polymerisation inhibitor and with full contact to water showed a beginning of polymerisation, which still remained minor (1%) (Figure 1).

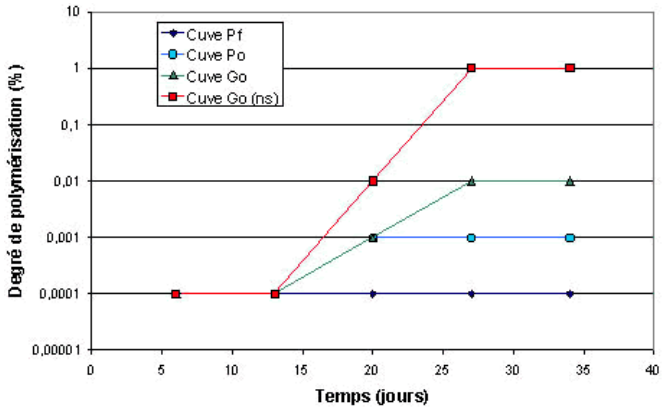


Figure 1: Polymerisation kinetics of styrene in the test tanks
©CEDRE

Regarding styrene mixed with polymerisation inhibitors (pTBC), no polymerisation process was noted. However, it is important to note that the concentration of pTBC considerably decreased for styrene in open tanks (Figure 2).

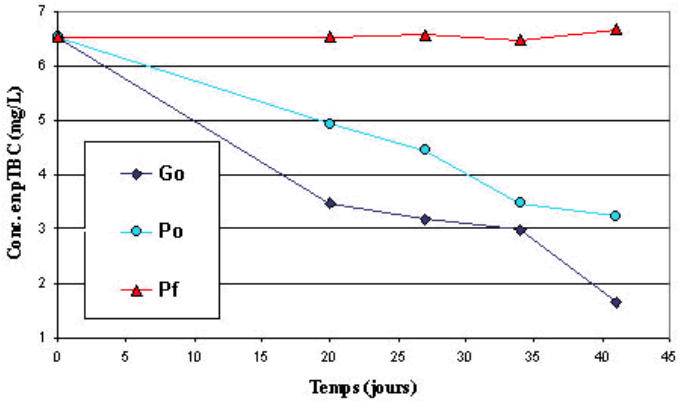


Figure 2: Evolution of pTBC concentrations in the test tanks
©CEDRE

In a laboratory:

After 10 days of immersion in 30°C water (temperature where polymerisation processes are quicker to appear), the styrene contained in the beakers did not polymerise, whether agitated or not.
After 70 days, both styrene volumes showed polymer levels slightly above 1%.

Immersion of stainless steel tanks in an outdoor sea water basin ©CEDRE

Control of the product's polymerisation ©CEDRE

Styrene: ecotoxicity tests and organoleptic tests carried out in CEDRE's infrastructure

1st test

It was proven that crabs exposed to styrene concentrations of 4 ppm for a period of 200 hours presented pollution levels (flesh and gills) between 5 and 15 ppm (see Figures 1 and 2).

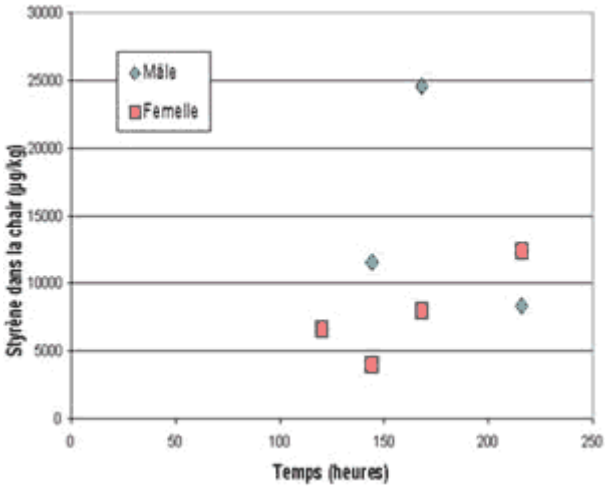


Figure 1: Styrene levels of crab flesh ©CEDRE

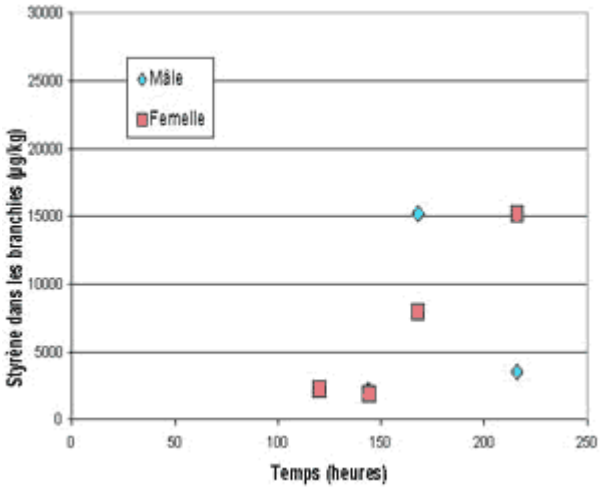


Figure 2: Styrene levels of crab gills ©CEDRE

In addition to these analyses, olfactory tests were carried out in the olfactometry laboratory of the Institute for Nuclear Safety and Protection (IPSN).

The exposure of crabs to styrene was effective since concentration in their flesh rose up to 24,600 µg/kg. These olfactory results from the IPSN study showed that the styrene smell was easily noticeable in these conditions. The control crabs were perfectly identified as not contaminated, as for crabs exposed to styrene, identified as contaminated.

Therefore, from a concentration of 5,000 µg/kg (5 ppm), it is possible to detect with certainty the presence of styrene by smell.

2nd test

The contamination period was of 8 days with a sampling of animals at various times, for analyses and transfer to decontamination tanks. Decontamination was also studied on a maximum period of 8 days.

The tests in the laboratory in Rouen showed that exposed crabs had contamination levels between 10,100 and 22,100 µg/kg for the flesh and between 3,200 and 33,000 µg/kg for the gills. The control crabs were not contaminated and showed less than 1 µg/kg. Following decontamination of 144 hours after exposure times of 48 h and 148 H, styrene was still detected, at respectively 20 and 121 µg/kg for the flesh.

Laboratory in Rouen ©CEDRE

Analyses of styrene contamination in crabs ©CEDRE

treatment of the wreck

The wreck of the *Ievoli Sun* was located and confirmed on 1November, by the sonar, then by the PAP of the French Navy's minehunter *Céphée*. This operation also confirmed the integrity of the ship. It rested on its port side at an angle of 120° 90 m deep, on sand and small rocks in an area subject to strong currents.

On 8 November, the *Northern Prince*, funded by insurers of the *Ievoli Sun*'s shipowner, carried out a full survey of the wreck using a submarine robot.

Various options were given by the insurers for the treatment of the cargo (chemicals and oil). They were reviewed by an experts committee made of representatives from:

- the Ministry for Transport
- the Ministry for the Environment
- CEDRE
- Ceppol

With the approval of British and French authorities, the charterer and its P&I Club hired Smit Tak Co on 10 April 2001 to operate on the cargo of the *Ievoli Sun*.

The operations were estimated to last 6 weeks. They were carried out by the *Smit Pioneer*, a multi-task vessel owned by SMIT International. Two recovery barges were stored on deck to recover the pumped products: one barge of 2,000 m^3 for the collection of styrene, the other of 370 m^3 for heavy fuel oil (IFO 180). Monitoring on the area was assured by the *Ailette*, a pollution response vessel, sent by the French Navy. The operations were carried out in 6 phases:

- Evaluation of the bunker
- deployment of base platforms and drilling of the outer hull of the *Ievoli Sun*
- assessment of the space between hulls
- drilling of the inner hull and direct release of MEK and IPA at sea, operation carried out with a controlled flow

- pumping and storing of styrene on the *Smit Pioneer*, later transferred aboard the chemical tanker the *Angela*. The transfer was carried out in a sheltered bay on the South of Great-Britain
- final assessment of the wreck and work area using a ROV (Remote Operated Vehicle).

The operations started on 12 April 2001 and ended on 31 May 2001, after 51 days of operations completely carried out by robots in harsh weather and sea conditions.

Other incidents implicating styrene release

The global production of styrene exceeds 10 million tonnes per year, it is therefore one of the most widespread base material for the production of resins and plastic. It is constantly transported in large volumes, by land or by the sea. Numerous industrial complexes store it in tanks, barrels, or cans. The incident risks are therefore considerable and data bases on leaks and incidental spills of chemicals all contain multiple examples of incidents involving styrene. However, these data bases are often incomplete and very succinct. They mostly include incidents in developed countries such as the USA, Canada, Japan, France. Therefore, an incident such as the one involving the chemical tanker *N° 1 Chung Mu* in South Chine (1995), for which CEDRE had been mobilised, would not be listed anywhere.

To our knowledge, no incident led to a situation similar to the incident of the *Ievoli Sun*: a large quantity of monomere styrene trapped in a wreck. This doesn't mean that such a situation never occurred before. But those who experienced it , if it happened, did not think it useful to communicate with the international community on it.

Available below are incident reports from CEDRE and data found in files we were given access to.

France

On 15 October 2000, an impact on the floodgate of Fresnes-sur-Escaut, near Valenciennes, led to a leak of about fifty cubic metres of styrene from one of the 10 180 m^3 tanks aboard a barge arriving from Belgium. Marine firefighters carried out diving operations to repair the leak while booms were installed downstream to protect the Scheldt from pollution. 14 people living in three houses near the area were evacuated for a couple of hours. 4 children suffering from skin irritation, were hospitalised but were cleared quickly (source: "Face au risque" magasine, n°364). CEDRE was not deployed during this incident and therefore does not possess data one potential impacts on aquatic flora and fauna.

China

On 9 March 1995, the container ship *N°1 Chon Stone* collided with the *N°1 Chung Mu*, a chemical tanker of 3,500 gross tonnage carrying monomere styrene, in the access canal for the port of Zhanjiang (South China).

On 5 February 2000, a styrene spill was declared after an HGV incident in the administrative region of Hong-Kong. A spill was noticed in the Mai Po protected area through rainwater systems, as well as non-quantified fish mortality.

Canada

About 11 tonnes of styrene were accidently spilled in a port environment, during loading and unloading operations, by the chemical tankers *Stolt Castle* (Québec, 22 December 1980), *Silver Magpie* (Sarnia, 29 September 1981), *Stolt Sydness* (Montréal, 19 April 1983).

Japan

After another vessel allided with it near Shimokita, on 23 June 1988, the chemical tanker *Sakura*, with a cargo of 20,000 tonnes of styrene, methanol, and ethylene dichloride, spilled 235 tonnes of styrene at sea from a damaged tank of 1,335 m^3, above the floatation line. The product spilled evaporated in a couple of hours, without polymerisation. There was no impact on the coastline of on marine resources.

Another incident, on 14 March 1988, near Nojima, involved the chemical tanker *Maasgusar*, loaded with 36,000 tonnes of 10 different chemicals, including 2,000 tonnes of styrene. No additional data is available.

Sources: exchanges with the Japanese centre for maritime disaster prevention and the Japanese Institute for research on vessels.

USA

The NOAA website details the pollution incident of the *Kathie G* barge in the USA on 8 September 1988. With 3,500 tonnes of styrene as cargo, the barge ran aground around midnight in the Mississippi, 140 nautical miles North of Bâton Rouge (Louisiana) and lost between 200 and 800 tonnes of product. Strong smells and respiratory issues were reported in the area. The following day, the product spilled quickly polymerised under the effect of the sun. Booms were deployed up to 30 miles downstream and 4 intoxicated people received medical assistance. The NOAA organised information campaigns for the public and local medical personnel, mostly regarding water drinkability.

a similar incident happened on the Louisiana coastline canal on 26 January 1992, after two barges had collided. One of them, transporting more than 14,000 tonnes of styrene, lost almost all of its cargo. The canal section was closed, strong smells could be noticed for more than 10 days and a marsh area was heavily polluted by a partially polymerised product. The incident was an occasion to confirm that monomere styrene was detectable on water using infra-red sensors, which matches

observations from the infra-red sensor of the POLMAR 2 aircraft on the product from the *Ievoli Sun*.

Three other minor spills were recorded in the USA:

- A spill of 650 litres of styrene in the sewer system by an industrial company in Philadelphia (Pennsylvania) on 13 August 1986;
- a spill from tanks containing styrene, xylene, and ethyl-benzene in Chesapeake (Virginia) on 3 August 1987;
- A train derailment caused the spill of 56 m^3 of styrene in Ohio river near Louisville (Kentucky) on 19 December 1996.

The documentation made available to CEDRE did not contain information on evacuation measures or containment of the population, nor impact studies on aquatic flora and fauna.

Similar cases involving oil pumping

This technique, not chosen for the *Erika* incident since it required technically challenging reheating of the oil, is adapted to the styrene contained in the wreck of the *Ievoli Sun*, which did not require reheating. We also have strong previous example, three of which are detailed below.

Recovery of the bunker of the Estonian vessel ***Estonia*** (1996 - Baltic Sea)

The *Estonia*, a 21,794 gross tonnage ferry, of 157 m in length and 24 m in width, was overturned during severe weather in 1996, leading to the death of 852 people. The wreck rested on its side, 60 m deep. The maximum amount of oil contained in the wreck was estimated to 418 tonnes. The decision was made to empty the bunker by pumping the fuel, before covering it with a concrete coffer to protect the remains of the 700 victims. However, this last operation was delayed by request of the families of the victims.
The pumping operations for the bunker of the *Estonia*:

- required no divers,
- were fully remote operated using multiple ROVs and an ROLS (Remote Operated Off Loading System),
- mobilised 2 dynamic positioning vessels, including one for rescue,
- lasted 42 days,
- cost 6MF (about €4.6 M),
- allowed for the recovery of 258 tonnes of oil,
- were carried out by the Frank Mohn AS company (ROLS), the Northern Engineering AS company (ROVs), the Taifun Engineering Oy company (pumps), and the Alfons Hakans Oy company (tugs).

Lightering of the South-Korean oil tanker *Yuil-n°1* (1998 – South-Korea)

The *Yuil-n°1*, a 1,591 gross tonnage oil tanker, long of 80.75 metres and wide of 12 metres, sank during towing after she had run aground. She sank 70 metres deep 1 mile from the coast and rested on its side. The vessel was carrying 2,870 tonnes of heavy fuel oil, part of which spilled during the incident. The maximum amount of oil still in the wreck was estimated to 1,400 tonnes.
Pumping operations for the bunker of the *Yuil-n°1*:

- required no divers,
- were completely remote operated using ROVs and an ROLS,
- mobilised 1 barge anchored to 4 lines, 2 support and pollution response vessels,
- lasted 60 days,
- cost 40.7MF (about €8.2 M),
- allowed for the recovery of 665 tonnes of oil,
- were carried out by the Smit Tak company, supported by the Frank Mohn AS (ROLS) and Racal Survey (ROV) companies.

Lightering of the South-Korean oil tanker *Osung-n°3* (1998 – South-Korea)

The *Osung-n°3*, a 1,115 gross tonnage oil tanker, long of 70.30 metres and wide of 10.50 metres, sank after she had run aground. The vessel sank 80 m deep and rested straight on its keel. The vessel was carrying 1,614 tonnes of heavy fuel oil, part of which spilled during the incident. The maximum amount of oil still in the wreck was estimated to 1,400 tonnes.
Pumping operations for the bunker of the *Osung-n°3*:

- required no divers,
- were completely remote operated using ROVs and an ROLS,
- mobilised 1 barge anchored to 4 lines, 2 support and pollution response vessels,
- lasted 69 days (with interruptions),
- cost 7.4MF (about €7.5 M),
- allowed for the recovery of 27 tonnes of oil,
- were carried out by the Smit Tak company, supported by the Frank Mohn AS (ROLS) and Racal (ROV) companies.

As for the previous case, the documents available precised that end-of-works reports were established, attesting that there were only a few cubic metres of fuel remaining in the wrecks. Estimates for the amounts trapped in the wrecks were therefore widely overestimated, which is frequent: the assessment of the spill during the incident was often below real amounts and a wreck that is not regularly monitored could continue leaking without being noticed. The wrecks remained where they sank based on those reports.