Bundesstelle für Seeunfalluntersuchung
Federal Bureau of Maritime Casualty Investigation
Federal Higher Authority subordinated to the Ministry of Transport,
Building and Urban Affairs

Investigation Report 304/06

Marine Casualty

Spillage of harmful substances from a container on board CMS HANJIN LONDON with 8 injured persons in the Port of Hamburg on 10 July 2006

15 May 2007

The investigation was conducted in conformity with the law to improve safety of shipping by investigating marine casualties and other incidents (Maritime Safety Investigation Law - SUG) of 16 June 2002.

According to this the sole objective of the investigation is to prevent future accidents and malfunctions. The investigation does not serve to ascertain fault, liability or claims.

The present report should not be used in court proceedings or proceedings of the Maritime Board. Reference is made to art. 19 para. 4 SUG.

The German text shall prevail in the interpretation of the Investigation Report.

Issued by:
Bundesstelle für Seeunfalluntersuchung - BSU
(Federal Bureau of Maritime Casualty Investigation)
Bernhard-Nocht-Str. 78
20359 Hamburg
Germany

Head: Jörg Kaufmann
Fon: +49 40 31908300 Fax: +49 40 31908340
posteingang-bsu@bsh.de http://www.bsu-bund.de

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1 Summary of the Marine Casualty

At about 07.10 a.m.[1] on 10 July 2006, at the Predöhlkai 1 berth in the Port of Hamburg, on board the container vessel HANJIN LONDON sailing under Korean flag, a spillage of 40 to 100 kg harmful substances occurred from a tank container, which was stowed on deck on the forecastle. These harmful substances were titanium dioxide and hydrochloric acid. These substances were formed when the cargo of titanium tetrachloride (UN-Nr. 1838) carried in the container reacted on humidity. Whereas the titanium dioxide precipitated as harmless powder, the hydrochloric acid escaped as a gas into the atmosphere. Thereby 2 crew members and 6 dockers were injured, and admitted to hospital by ambulance. After the inhalation of vapours of hydrochloric acid, a formation of enduring lung oedemas may occur. All of the injured persons could be released from the hospital after a short inpatient treatment.

[1] Any times given in the report are in CEST = Central European Summer Time = UTC + 2h

2 Scene of the Accident

Type of event:	Marine Casualty
Date/time:	10 July 2006, 07.10 a.m.
Location:	Port of Hamburg, Predöhlkai 1
Latitude/longitude:	φ 53°31,5' λ 009°55,6‘

Section of Chart 3010, Page 11, Federal Maritime and Hydrographic Agency

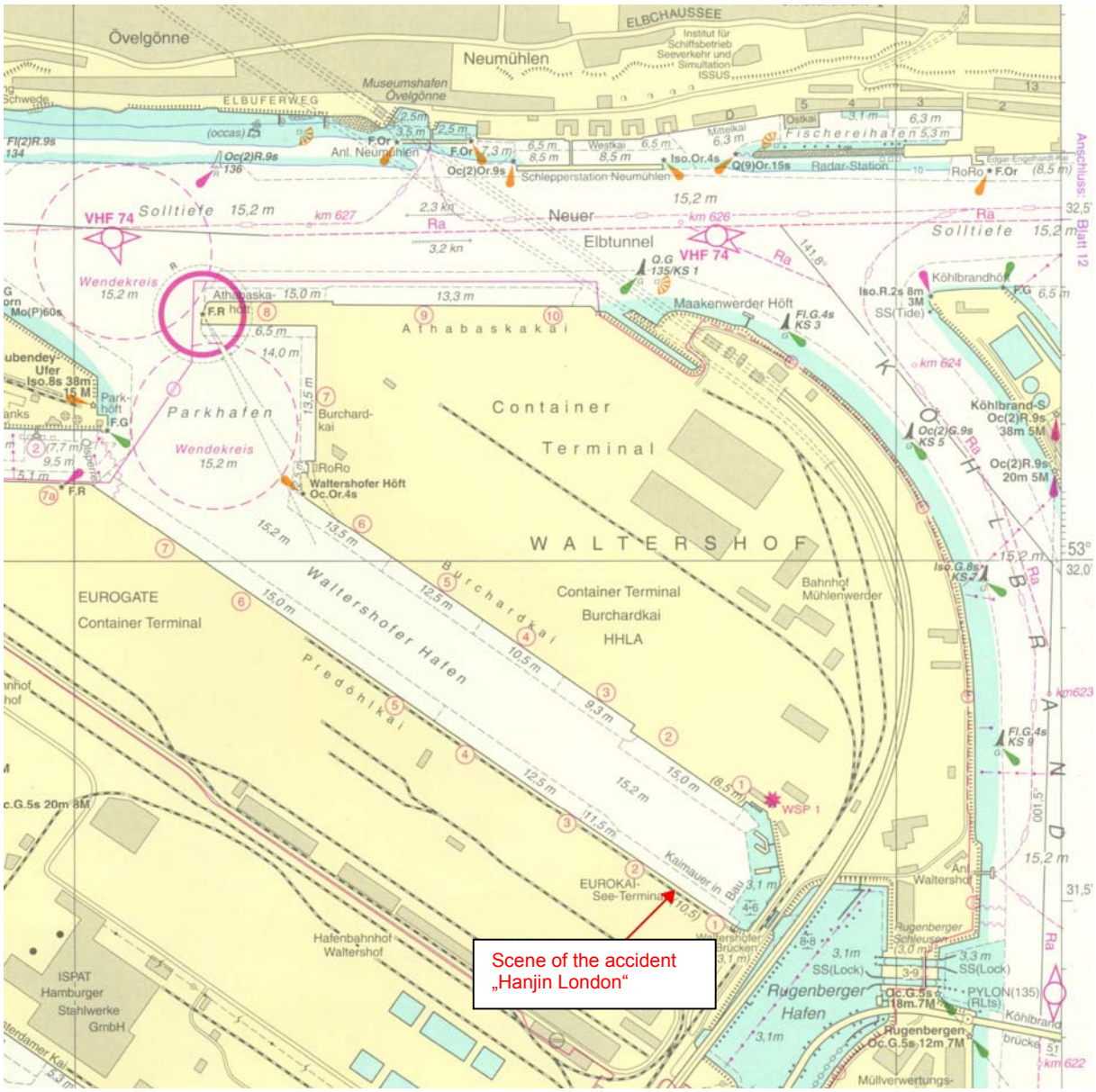

Figure 1: Chart

3 Particulars of the Vessel

3.1 Photo

Figure 2: Photo of the vessel

3.2 Particulars

Name of the vessel:	HANJIN LONDON
Type of the vessel:	Container vessel
Nationality/flag:	South Korea
Port of registry:	Jeju
IMO number:	9111383
Call sign:	DSEI7
Vessel operator:	Hanjin Shipping Co. Ltd.
Year built:	1996
Shipyard/number:	Hanjin Heavy Industries Co. Ltd., Pusan
Classification society:	Korean Register of Shipping (KR)
Length over all:	279 m
Breadth over all:	40.41 m
Gross tonnage:	66687
Displacement:	67298
Draught, constant:	14.02 m
Engine rating:	74494 HP/54809 kW
Main engine:	2SA12CY
Speed:	26.3 kn
Hull material:	steel

4 Course of the Accident

HANJIN LONDON was on her voyage from Rotterdam to Hamburg. The container, which had been filled with titanium tetrachloride (UN No. 1838) in France, was stowed on deck on the forecastle in Rotterdam (see fig. 3) and bound for Korea. When gas escaped from the container at the berth in Hamburg, the container was set ashore (see fig. 4) and deposited in a vat designated for harmful substances at the gas application site with the Eurogate company. At about 10.40 p.m. on July 11th, the company DOW Chemical started pumping off the remaining cargo. At 00.30 a.m., the pumping was completed. When measuring the cargo, a loss of 40 to 100 kg was detected. On July 12th, 2006, the damaged container was transported to the company Remain in Hamburg. There it was neutralised and cleaned under the supervision and instruction by employees of the French manufacturing company, in order to make it accessible for the inspection scheduled for July 17th, 2006. On the day of the inspection, the company Dr. Fintelmann and Dr. Meyer still detected some residues of the cargo. Therefore, for the time being, parts of the panelling and insulation (see fig. 5) of the container were removed. During this work, portions of the cargo again leaked from one of the heating pockets and from a heating tube. After repeated cleaning and disassembly of a standpipe, the container could be inspected by Germanischer Lloyd on July 18th, 2006. On this occasion, sites of previous repair work and other holes in the heating system (see fig. 7) were found in the tank (see fig. 6) and in the area of the heating pockets. Initially it was supposed that the cargo got into the heating system of the container and from there outwards through the holes. However, no statements could be made on the causes of the holes or corrosion, respectively .

Figure 3: Row of containers

Fig. 4: Evacuation to the gas application site

Fig. 5: Removal of the insulation

Fig. 6: Sites of previous repair work

Fig. 7: Eroded pipe in the heating system

5 Investigation

The investigation report refers to the expertise ordered and the investigations held by the waterways police of Hamburg (WSP) as well as to the investigations by the BSU.

5.1 On Call and Rapid Intervention Information System (RESY) of the WSP

Titanium tetrachloride, chemical formula $TiCl_4$, has the UN No. 1838, and according to the RESY of the WSP has to be classified as class 8 and Packing Group II. It is an inorganic halogen compound and is used as a mordant in textile industry. The substance is a colourless to yellow liquid, and its smell is sharp and choking. The liquid is highly corrosive and reactive. It is mostly combustible, but not easily inflammable. There is a danger of a flashback with combustible and toxic vapours in a vessel. Serious and enduring damages to health may develop in form of pulmonary oedemas at a delay of up to 2 days. In case of exposure to the liquid, serious chemical burns of the eyes, skin, and respiratory passages are possible. The substance reacts with water. As personal protective equipment, a full protective clothing with a breathing apparatus with independent air circulation is required (see fig. 8). In case of leakage, the substance must be contained and pumped off as well as kept away from

humidity. Small amounts can be washed off with lots of water, and any remaining amounts can be neutralised by means of lime powder.

Fig. 8: Operation using protective clothing and breathing apparatus

5.2 Measurement and Survey by Company Dr. Fintelmann and Dr. Meyer GmbH

The container was located on the premises of the company Remain and had been neutralised by means of caustic soda and then flushed under high pressure. At the first visit on July 17th, 2006, 10 ppm[2] of hydrochloric acid portions were still found inside the container and in the insulation, in addition, some white and yellow residues on the bottom of the container and in the area of the standpipe. Therefore, the residues were washed by means of a high-pressure cleaner, and the insulation was removed as far as necessary. In addition, the standpipe was dismantled. The next day, the measurements in the interior showed 20.9 % of oxygen and 0 ppm of hydrochloric acid portions. The container was free from removable residues. Serious discolouration and erosions were visible throughout the container. Two holes were detected in the bottom (see fig. 9). On a heating channel welded onto the tank, white efflorescences and slight vapours of hydrochloric acid were visible on the outside. An attempt to purge the heating channels under high pressure failed, as the channels were obviously blocked. The efflorescences that had appeared were removed once again.

[2] ppm = parts per million

Fig. 9: Holes in the bottom

5.3 Survey and Examination Certificate by Germanischer Lloyd

The container was empty and cleaned. The insulation and cover were removed for large areas of the surface, and the heating pipes had been purged as far as possible. Various sites of the frame, the welding seams as well as the inlet and outlet pipes were corroded (see fig. 10 and 11). The profiles of the frame showed deformations in the area of the upper and lower longitudinal beams. Cracks were detected in the welding seam and in the upper longitudinal profile at the connection with the upper transverse beam. Some welding seams in the circumferential stiffening ring of the tank body were cracked. In the area of the outer stiffening ring, the insulation and its fixation did not correspond to their original condition. 3 leakages or cracks, respectively, that could be seen from the outside were detected on the heating system. They were in the pipings in the inlet and outlet area as well as in one of the lower heating shells on the vacuum stiffening. Inside the tank, three other cracks were detected in the lower part of the heating body. During the inspection, liquid leaking from the heating shells entered the tank body and accumulated on the cylindrical floor.

Fig. 10: Inlet socket

Fig. 11: Welding seams

5.4 Examination Report by the Institute for Material Research and Welding Techniques (IWS)

The IWS was charged to ascertain the causes of the leakages, taking the examination reports and the photos taken as a basis. The tank container ETNU 150005-1 was built in 1996. It consists of material AISI 316Ti (German material number 1.4571). In certain concentration ranges, this steel is resistant to alkalis, nitric acid and sulphuric acid. But it is not resistant to hydrochloric acid. In case of a reaction on hydrochloric acid, pitting corrosion and stress corrosion can occur.

The tank is insulated on the outside and equipped with a tank heating, which is welded onto the outside wall in the form of pipe half shells. The material of these shells seems to be of the same type. In addition, a stabilising ring in the form of a rectangular pipe was placed around the tank, which must be considered as a pressure vessel, and welded onto the tank.

The container was used for the transport of different products. Thus, in an offer for repair work dated 25 October 2000, “Sulfonic Acid” is mentioned as previous cargo, in another offer dated 8 October 2003 “Sulphuric Acid”, and in a third one dated 14. January 2004 again “Acide Sulphurique” (sulphuric acid). Assuming examination intervals of 2.5 years, it results that obviously sulphuric acid was transported before the last inspection.

All of the three offers include the indication that a small amount of pitting corrosion was present, which was due to be ground or polished off, respectively. The offer dated October 2003 also mentions three holes that should be repaired by welding. There is no such indication of holes in the offer dated January 2004 .

It could not be reconstructed whether, and when which repairs were performed on the container. The last product transported was titanium tetrachloride. In June 2006, the tank underwent a routine inspection by the Bureau Veritas classification society. According to the report No. 1009658/Cont/06/087/69/228/HJU, this inspection included the following items:

- Inspection of the tank from the inside
- Inspection of the not insulated tank from the outside
- Check of the valve settings
- Check of the equipment
- Leak detection
- Test of the heating
- Test of the frame
- Verification of the labelling

Then the leakage occurred on July 10th, 2006. Since, the container was repaired and again put into service. Samples for examination are no longer available.

The inspection of the inside of the tank shows many welding seams. This is at first due to the fact that the tank was cleaned with water and that the leak detection test was performed with water. Thereby, residues of the product can react on the water, and the resulting acid will slightly etch the surface of the tank, so that the welding seams will become visible. In this process, a small amount of material will be taken away as well. But no rust will be caused, as the corrosion products will remain dissolved.

The areas of corrosion are mainly affected by pitting corrosion. The edges of the corrosion holes, which are sharp on the inside of the tank, suggest that the corrosion started from the side of the heating. Some of the pictures reveal that the holes are located at the end of each welding seam. The form and positions of the holes suggest end crater-type flaws. A defective spot, in contrast, is not a hole, but an extended leakage with partly cracked appearance. The appearance of this leakage is attributable to a lack of fusion or a slag inclusion. Thus, it is very likely that the corrosion holes are connected with flaws in welding. By these welding flaws, the occurrence of the leakage was considerably accelerated.

There are cracks in the stiffening ring. In the area of the cracks, no deformation can be seen. As with the given material a brittle fracture and with the given working conditions a fatigue fracture must be excluded, these are probably caused by stress corrosion. The leakage into the heating pipes should also have been due to stress corrosion.

Titanium tetrachloride itself does not cause any corrosion on the given type of steel. A corrosion can only occur if water is added to the titanium tetrachloride. A slight reaction has to be expected if atmospheric moisture cannot be excluded. This corrosion would mainly occur on the surface of the product.

In the present case, water was obviously in the heating channels, and a product was left in the tank. The product must have entered the heating channels, where it caused the corrosion (see fig. 12). This requires a primary point of leakage. From the records and documents submitted, it can no longer be understood which was the primary point of leakage. Thus, the primary cause of the damage cannot be identified any more.

Fig. 12: Eroded pipe leading to the heating system

Another reflection results in the following:

Before the tank container was cleaned due to the scheduled inspection, no damage seems to have existed. This however, does not result in the conclusion that no damage existed, instead that at this time no water was in the heating pipes. During the cleaning work on the tank, water could have entered the heating pipes via an already existing leakage. This should have been detected in the leakage and heating test.

It is obvious that the damage occurred as a consequence of an inspection. By each inspection, a corrosion can be caused by previously cleaning the container with water.

It is to be assumed that after the inspection water was left in the heating system, and there was a leakage that resulted in a damage. The damage was caused by the fact that the water in the heating channels had mixed with the product.

Finally it could not be clarified how the inspection was performed. It is possible that after the leak detection and heating test, the tank was not inspected to a sufficient extent or even not at all. One could also imagine that a leakage was in the tank which was not found at the leak detection test; this would happen in case the heating channels were closed off during the test .

For the transport of titanium tetrachloride, no heating is required. Therefore the channels of the heating should have been drained after the examination of the tank, as otherwise there would have been a danger of pitting corrosion.

5.5 Examination of the Tank Container by Bureau Veritas

The tank container ETNU 150005-1 was taken to the inspection bureau of Cie LES Services of Mornant (Rhön) for the purpose of the inspection due every 2.5 years, which was scheduled for 15 June 2006 . This test was performed according to the BV procedure with respect to the periodical inspection of tank containers and set-down tanks.

During this examination, the following items were checked, among others :

In the check of the inside, no defects were detected which had to be objected concerning the safety of the tank. In this connection it must be taken into consideration that the inside of tanks often is ground. Therefore, the search for a possible repair is difficult. In addition it must be pointed out that the tank was insulated and the outside of the tank was not visible.

The external inspection of the insulation did not show any particular indications, no dents and no rests of any products which would have called the examiner's attention to possible damages on the tank.

The leak detection test of the tank was performed at a pressure of 1.5 bar[3] after the pressure had been stabilised. This check was done with a type of soap, and at the same time it was checked whether a loss of pressure occurred on the manometer .

In the check of the steam heating, no leakage could be detected. If the steam coil had been leaky, any leakage would immediately have been identifiable by means of the loss of pressure on the manometer due to the small volume of such a steam heating. This inspection was performed according to the Annex to the BV procedure, Section 14. As the container was insulated, no visual inspection of the external tank could be performed.

Concerning the leakage problems, Bureau Veritas declares the following:

An undetectable old crack or an old repair was opened during various container transhipments. This crack or these cracks, respectively, developed at the points where the steam heating is welded.

The liquid circulated through the heating system. As the product contained titanium tetrachloride UN1838 (a substance reacting on water), a chemical reaction of this product with the remaining water in the steam heating was caused. By this, corrosion

[3] According to the statutory regulations on dangerous goods, within the scope of a regular test at an interval of 2.5 years, only a leak test at 0.2 bar minimum is required, and not before the quinquennial test the tank undergoes to the hydraulic pressure test at its nominal test pressure indicated on the tank label . For this reason, the leak test on the above mentioned tank container was performed at a test pressure of 1.5 bar.

could have been occurred on the coils of the steam heating. This damage resulted in a leakage in the steam heating.

Grinding marks on the outer surface of the heating coil were not inspected during the examination, as the tank was insulated. As the leak detection test showed a regular result, a removal of the insulation was not considered necessary. Nevertheless, there is a possibility that the heating system was leaky, after corrosion had occurred on the weakest point of the heating coil.

The container could possibly have been damaged by a heavy impact and presented separations of welding seams on the longitudinal beam. This impact could be the cause of the cracks and of the leaky point that occurred later. This damage was not present after the inspection due every 2.5 years, when the container left the inspection bureau.

When leaving the examination centre, the container was completely tight. After that, an incident causing the leakage (impact, improper handling, etc.,) must have occurred.

5.6 Structural Safety Requirements and Tests for Containers

In the CSC (International Convention for Safe Containers) regulations were established for the testing, inspection, approval and maintenance of containers. Except for the maintenance, in many countries classification societies are commissioned with these tasks. Each container must have a CSC approval. The interval from the date of manufacture to the date of the first examination shall not exceed five years. Subsequent examination of new containers and re-examination of existing containers shall be at intervals of not more than 30 months. All examinations shall determine whether the container has any defects which could place any person in danger.

The owner of an approved container shall examine the container or have it examined in accordance with the procedure either prescribed or approved by the Contracting Party concerned, at intervals appropriate to operating conditions. Some years ago, the check of the container has mostly been passed into the owners' responsibility. This is the object of the so-called „Approved Continuous Examination Program" (ACEP). This is an approved repair and maintenance system with inspections and the correction of faults at regular intervals. Of course, in this case, it falls within the owner's responsibility to provide for the required examinations. Then the indication of the date of an examination on the CSC safety approval plate is unnecessary.

5.6.1 Tank Container

The IMDG Code (International Maritime Code for Dangerous Goods) describes 8 types of tank containers. IMO Type 1 designates a mobile tank for the transport of substances of the classes 3 to 9, equipped with pressure relief equipment, with a maximum allowed working pressure of 1.75 bar and above (see figs. 13 and 14). Titanium tetrachloride belongs to Class 8 (Corrosive Substances) and the Packing Group II (Medium Danger). Packing Group II is assigned to substances which during an observation period of up to 14 days after an action of more than 3 min, but 60 min at the most, cause a destruction of the unharmed dermal tissue over its complete thickness. The substance is colourless, liquid and briskly reacts on water producing hydrogen chloride, a corrosive gas with an irritating effect. The gas can be seen as a white fog and heavily corrodes most of the metals. The steam has irritating effects on mucous membranes. The stowage (Category C) must be done on deck and away from watch and common rooms. Substances of the class 8 must be kept as dry as possible, because they briskly react with water. For the transport, a tank container must be used which sustains a minimum test pressure of 4 bar and shows a minimum wall thickness of the tank body of 6 mm. No opening in the bottom are allowed. A heating for the tanks for the maintenance of minimum temperatures is not prescribed.

Fig. 13: View of the outside and marking of the tank container

Fig. 14: View of the inside of the tank container

6 Analysis

Based upon the submitted expertises, it could not be clarified when a chemical reaction of the product titanium tetrachloride (UN No. 1838) with the water in the steam heating has taken place. It was no longer possible to identify the point of the initial leakage and thus the primary cause of the damage. However, it is beyond doubt that a reaction on the cargo took place.

The damage was caused, above all, by the fact that water was in the heating pipes, which mixed with the product. For the transport of the cargo, no heating of the cargo is required. Therefore the heating system could have been completely emptied, in order to prevent, from the beginning, the risk of mixing with the cargo.

In the examination procedure of the dangerous goods container, the BSU could not detect any safety breaches. Finally any check can only confirm that at a given time, the test item is faulty or free from faults. There cannot be any unlimited certainty on the proper functioning of the test item after the check. In addition, any excess inspections and any inspections performed improperly, if applicable, can additionally wear the test item. It is only the extents of such accidents that can be reduced by means of risk analyses and preventive measures.

Based upon the records it could not be finally clarified to what extent the company Eurotainer had repairs done on the tank container before the examination, and what kind of repairs. According to an existing quotation dated 14 January 2004, probably not all of the recommended repairs were performed. In the quotation it was noted, among others, that the surface of the tank showed damages by corrosion and that previously sulfonic acid and sulphuric acid had been transported. According to the statement of Bureau Veritas it is difficult to determine any previous repairs by a visual examination. Here it must also be referred to the operator’s responsibility. According to the IMDG Code as well as the German Maritime Dangerous Goods Regulation, sufficient maintenance of the containers must be guaranteed.

7 Safety recommendation(s)

The Federal Bureau of Maritime Casualty Investigation recommends the operators and the shippers of tank containers, in case of a change of the cargo to check whether the additional function “heating” is required for the transport and which dangers to the transport could originate from the type of the heating. The tank container of the IMO Type 1 is a construction type that is allowed for use with many cargoes of the Hazard Classes 3 to 9 and that is very common. In case of heating systems that are run with liquids, the heating system should completely be emptied, if necessary, in order to prevent any chemical reaction on the propellant and any resulting corrosion.

8 References

- Investigations and commissioning of experts
  Waterways police (WSP21, Environmental Offences) Hamburg

- Written Declarations/Opinions
  - Liability Insurance Company: Pandi Services J.&K. Brons, Hamburg
  - Hanjin Shipping Company, Hamburg
  - Classification Society: Bureau Veritas, Hamburg

- Expertises/Specialist's Contributions
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  - Germanischer Lloyd, Hamburg
  - Dr. Fintelmann and Dr. Meyer GmbH, Hamburg
  - Dr. C.-P. Kramer and Dr. H.-W. Meyer, Hamburg
  - RESY, Rufbereitschafts- und Ersteinsatz-Informationssystem (Standby and Rapid Intervention Information System), Water Police of Hamburg

- Charts and Particulars of the Vessel
  Federal Maritime and Hydrography Agency (BSH), Hamburg