DICH'T!
Trialog der Dichtungs-, Klebe- und Polymertechnik
POWER ENGINEERING  BONDING TECHNOLOGY, MACHINES AND SYSTEMS  If three giant LNG tankers are still safe on the oceans after thirteen years, an atmospheric plasma nozzle technology and the cooperation of Franco-German engineers in the implementation of the safety-relevant bonding process for tank insulation have made a decisive contribution to this.

According to experts, natural gas or LNG (Liquified Natural Gas) is one of the fastest growing energy sources in the world. LNG is produced by freezing natural gas to -161 to -164 °C, liquefying it at this temperature, and now, due to its increased density, having only one six hundredth of its volume in the gaseous state. In this compressed form it is ideally suited for storage in special LNG export and import terminals and for transport in tankers.

LNG, which consists mainly of methane, is colorless, odorless and non-toxic. It is also non-flammable, unlike the gas that develops in the gaseous state when heated, which can form explosive mixtures with a certain proportion of oxygen. LNG tankers are the flexible alternative to transporting natural gas in pipelines. Since they transport liquefied natural gas over long distances and in large quantities from their liquefaction terminals to the regasification terminals on the world's oceans, they must be extremely well insulated and absolutely leak-proof (Fig. 1). With membrane tankers, the heat of the outside air penetrating through the tanker wall must be kept as low as possible, since each heat supply leads to evaporation of the liquefied gas and thus to an increase in the internal pressure of the tank. The proportion of methane, the „boil-off gas“, which is constantly emitted despite all insulation measures, is removed from the tanks in a targeted manner and either used immediately as fuel for the ship or flared off in the atmosphere under high safety regulations. The membranes built into the insulation levels serve as barrier layers. Their primary task is to prevent the cold liquid natural gas from escaping through a leak and coming into contact with the steel structure of the ship's hull. Even the slightest leak could lead to embrittlement of the structural steel and destroy it.

The example of a worldwide unique application of this pretreatment method shows how long-term stable and permanently tight an originally non-adhesive bonding of the sealing layer after pretreatment with atmospheric pressure plasma (AP plasma) can be. Over a total length of more than 100 km, the plasma nozzle technology Openair-Plasma ensured the tightness of the insulation panels during the construction of the two largest LNG tankers at the time and their smaller sister ship in 2005 and 2006 (Fig 2).

The tankers can be divided into five main sectors. The engine room is located in the rear part of the ship. Four highly insulated tanks integrated into the hull and largely adapted to the ship's shape are arranged one behind the other in front of it. The membrane systems are not self-supporting; the double hull of the steel hull forms the actual supporting tank structure.

Membrane system CS1
The CS1 insulation technology developed by GTT (Gaztransport & Technigaz) was used for the first time in the construction of the three ships. It enables the complexity of the insulation layers and their thickness to be reduced so that the tanker capacity can be increased by 8,000 m³ while maintaining the ship’s size. Ship classification requires membrane tankers to have a double barrier against the passage of...
of liquid gas to the steel hull. The membranes are monitored by sensors. The overall construction of the CS1 system has four levels:

- **Barrier 1**: The inner, impermeable metal membrane forms the actual cargo container and is therefore in direct contact with the liquid natural gas (Fig. 3). This first barrier consists of a 0.7 mm thick, well insulating Invar steel, an alloy with a very low coefficient of thermal expansion. The stresses caused by the extreme temperature differences between the -163 °C cold gas and the 20 °C warm outer shell are thus compensated. Behind the steel membrane is an insulating layer of plywood and a 10 cm thick polyurethane foam.

- **Barrier 2**: A rigid “Triplex” panel follows. It is the actual characteristic of CS1 technology (Fig. 4), because until now the second barrier in membrane tankers has also been made of invar steel. Its task is to secure any leaks in the first, i.e. to prevent the extremely cold liquid natural gas from coming into contact with the steel wall of the ship’s hull in the event of a leak in the tank, which would lead to embrittlement fracture.

- **The structure**: This consists of two outer glass fiber components and a thin aluminum layer in between. Together with the flexible Triplex tapes to be bonded to seal the joints, the material composite forms the second impermeable membrane. Between the Triplex barrier and the inside of the double-walled metal hull of the ship lies another 20 cm thick layer of foamed polyurethane. The insulating composite material is bonded directly to the inside of the double metal hull of the ship.

**Construction start and stop**

Construction of the new tanker series began in St. Nazaire with Gaz de France Energy. Its scheduled delivery date was the end of 2004. But then a serious problem arose: the basically completed ship was suddenly found to have leaks in the second safety barrier (plastic composite) of the CS1 membrane system, which meant that the remaining work had to be stopped immediately. According to a report by the maritime news portal „Mer et Marine“ [1], it took months for engineers and technicians to determine the exact cause of the failure. Finally, the result was that the flexible Triplex tapes bonded for sealing the joints of the composite panels lacked sufficient adhesion.

Work also had to be interrupted on Provalys, which was already under construction at the time. Nothing could be done until a solution to the sealing problem had been found. For the shipyard, the consequences of the construction stops were immense: binding delivery dates could not be met, work was halted and contractual penalties amounting to millions were due.

**Cause of damage and solution**

If a suitable adhesive does not want to adhere to an additive-free plastic, it can almost certainly be assumed that its surface is either not really clean or that the surface energy is not sufficient for homogeneous wetting with the adhesive. In the case of the LNG tankers, both came together, but the main factor was the invisible pollution of the ambient air caused by the work. The ambient atmosphere in a test laboratory does not correspond to the real situation after all. The environmental conditions in shipbuilding are more similar to those on a large concrete construction site and it became clear that the bonding processes of the insulation work could only be continued using complex ventilation and air conditioning systems on the one hand, and that, on the other hand, pre-treatment of all bonding points was required. But finding the right method proved to be more difficult than expected. Neither pre-treatment with a primer nor flame treatment of the surfaces produced the desired adhesion result.

Here it was recalled that a plasma process for difficult bonding processes had already been successfully used in the French automotive
industry - Plasmatreat’s Openair-Plasma process. The evaluation of the technology showed that the plasma treatment not only produced the best adhesion results, but also fulfilled all environmental, safety and efficiency requirements. From now on things were moving ahead. In cooperation with the shipbuilder’s engineers and the machine specialists Servisoud and ASI, Plasmatreat delivered twenty „plasma robots” to Chantiers de l’Atlantique between March 2005 and April 2006, whose adaptability enabled them to process the enormous areas.

Step one - giant plasma treatment

The pre-treatment solution with atmospheric pressure plasma was the first large-area application of rotating plasma nozzles integrated in robots worldwide. The application was at the level of the second barrier. The aim was to prepare the bonding process for thousands of flexible Triplex tapes. The tapes had a width of 30 cm and a total length of approx. 40,000 m per large tanker. They were to be used to cover the edge seams of the 1 x 3 m insulation panels with a 2-component epoxy adhesive to ensure complete tightness.

For the pre-treatment process, the workers first fixed a 3 m long auxiliary rail for the robot in front of the work surface. After programming the start and end points, the robot controlled the exact workflow of the nozzle and moved it fully automatically at a speed of 6 m/min and a distance (nozzle head/surface) of 10 mm over the surface to be treated. Plasma exerts a multiple effect on plastic surfaces. On the one hand, micro-cleaning destroys all organic substances present on the surface. Loose dust particles are eliminated at the same time by the high outflow speed of the plasma. Since the plastic is also statically discharged by the plasma treatment, dust from the ambient air is no longer attracted. In addition, the plasma simultaneously activates the surface, i.e. modifies it at the molecular level. This has a positive effect on the adhesion properties of the material. Non-polar plastics become polar and their surface energy increases to such an extent that homogeneous wettability with an adhesive and its long-term stable adhesion are given (Fig. 5).

Step two: The bonding process

Pre-treatment and bonding could only be done piece by piece, which meant that the team had to remove the auxiliary rail after each pre-treatment process and rebuild it on the next surface to be treated. In a second step, immediately following the pre-treatment, another team carried out the actual bonding process: All panel edges, which had previously been finely cleaned and activated with plasma, were now adhesively covered with the Triplex tape to make them joint-tight.

The effort invested by the shipyard is reflected in the manpower used: Three hundred employees specially trained for the production of this insulation layer worked three times eight hour shifts around the clock and moved it fully automatically at a speed of 3 m/min and a distance (nozzle head/surface) of 10 mm over the surface to be treated. Plasma exerts a multiple effect on plastic surfaces. On the one hand, micro-cleaning destroys all organic substances present on the surface. Loose dust particles are eliminated at the same time by the high outflow speed of the plasma. Since the plastic is also statically discharged by the plasma treatment, dust from the ambient air is no longer attracted. In addition, the plasma simultaneously activates the surface, i.e. modifies it at the molecular level. This has a positive effect on the adhesion properties of the material. Non-polar plastics become polar and their surface energy increases to such an extent that homogeneous wettability with an adhesive and its long-term stable adhesion are given (Fig. 5).

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Facts for buyers

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Facts for designers

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• Laboratory tests can only be integrated to a limited extent into the practice – especially in the case of rough production conditions

Summary

With its plant technology, Plasmatreat has created a solution that enabled the surface treatment required for the Triplex bonding processes to be carried out directly on the construction site under the best conditions. While the Energy was delivered with a delay of about two years due to the long standstill, the large tanker Provalys started its maiden voyage in November 2006 with a delay of one year. The sister ship Gaselys had benefited from the new pre-treatment process from the start of construction and was launched at the beginning of 2007.

Although the three ships are the only tankers to date to be equipped with CS1 membrane technology [2], the close Franco-German cooperation in the emergency situation at the time has paid off and the high adhesion of the bonded joints achieved by Openair-Plasma technology has proven its long-term stability. Even after 13 years, the trio still ships huge quantities of ice-cold natural gas across the world’s oceans - and certainly for many more years to come. Unlike oil tankers, which are usually scrapped after 20 to 25 years, LNG tankers have a service life of more than 40 years.

Literature index:

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Further information

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