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Liquid gas transport economically and safely thanks to plasma pretreatment



USE OF ADHESIVES TECHNOLOGY IN GIANT LIQUID GAS TANKERS

Safer LNG transport due to correct pretreatment

The example of the transport of natural gas from remote production countries impressively shows once again the benefits – both economic as well as in terms of safety - that can be derived from the use of modern adhesive bonding technology. When the currently largest liquid gas tankers in the world cruise over the oceans both atmospheric-pressure plasma and adhesives as well as excellent German-French collaboration have made a decisive contribution to this.



Figure 1: Liquefied natural gas today is increasingly being transported unpressurised at $-163\text{ }^{\circ}\text{C}$.
(Photo: Rolf Müller-Wondorf)

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Despite increasing use of renewable energy from the sun, wind and water the economic importance of natural gas for use as a fuel in households, industry and commerce is also growing. By comparison with other fossil fuels natural gas is regarded as relatively environmentally friendly on account of its physical and chemical properties. It contains no substances like sulphur, fluorine or chlorine that give rise to pollutants and emissions of oxides of nitrogen and sulphur dioxide are low. The transport of natural gas from the most varied production countries is done for the most part via long-distance pipelines under a pressure of 65 to 70 bar.

When due to the great distances involved economic transport by the pipeline network is no longer feasible special tankers are used (Fig. 1). In order for natural gas to be transported by ship this energy source is first of all cooled down in liquefying plants in the far flung production countries to minus 163 °C. In this fashion the original volume is reduced to 1/600. At its destination the liquid gas is regasified and fed into the natural gas network of the consuming country.



Figure 2: To insulate the tanker CS1 insulation technology was employed for the first time. This allows reduction of the composition of the insulating layers and their thickness to such an extent that the capacity of the tanker was increased by 8,000 m³.

(Photo Yves Guillotin)

LNG (liquefied natural gas)

- Natural gas comes from underground deposits that have been produced over thousands of years by the rotting of vegetation and tiny creatures.
- Natural gas is lighter than air and burns at a gas concentration of 5 to 15 per cent in air. For ignition a temperature of 650 °C is needed.
- Natural gas remains gaseous down to a temperature of -162 °C. At lower temperatures it becomes liquid (LNG, liquefied natural gas) and reduces its volume by a factor of 600.
- Liquefied natural gas (LNG) is today increasingly being transported unpressurised at -163 °C in special tankers.
- At the destination port the liquid gas is first of all stored in storage tanks. In order to feed it into the pipeline network it is converted to the gaseous state by heating.

The order

The “Les Chantiers de l’Atlantique” shipyard (now renamed “Aker Yards”) in St. Nazaire in France is rich in tradition. It has built famous ships like the “Ile de France” and the world’s biggest cruise ship the “Queen Mary 2”. At the end of 2003 the shipyard was awarded a contract by the energy giant Gaz de France for building three LNG membrane tankers: the EnergyY together with the two sister ships Provalys and Gaselys. The latter two measuring 300 m in length, 42 m in width and 50 m in height were to be the largest gas tankers in the world.

The technical requirements are high. Thus, as little natural gas as possible should evaporate during transport. Furthermore, the steel structure of the ship must not come into contact with the cold liquefied natural gas in order to prevent embrittlement and hence destruction of the ship’s hull composed of normal constructional steel.

To ensure that this cannot happen a special insulation system applied with the aid of adhesive bonding technology is needed in the interior of the tanker. The insulating material must provide a reliably tight seal, i.e. it must not fail at the low temperature of – 163 °C.

The task

The new CS1 insulation technology developed by GTT (Gaztransport Technigaz) was to be used for the first time for insulating the tanker. This technology makes it possible to reduce the composition of the insulating layers and their thickness to such an extent that the capacity of the tanker can be increased by 8,000 m³ (Fig. 2).

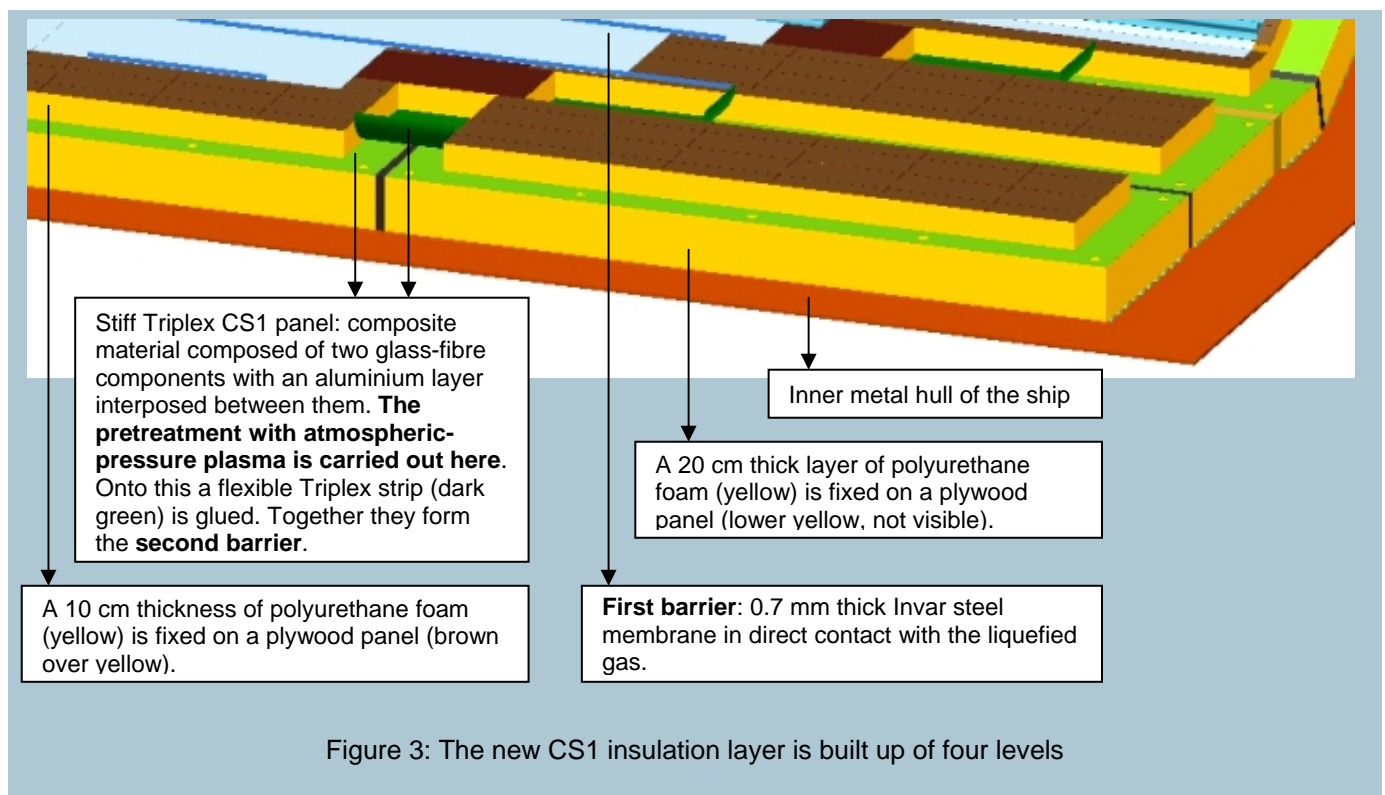
In doing this the aim was to ensure absolute leak-tightness in bonding the new composite insulation panels directly to the inner ship's wall.

In order now to meet all the requirements imposed, Aker Yards – after extensive tests on other systems - bought for about one million Euros in spring 2005 twenty robot-controlled atmospheric-pressure plasma systems from the company Plasmatreat. These systems are used for ultrafine cleaning, activating and coating the surfaces of materials.

The membrane tankers Provalys and Gaselys have four individual tanks with a total volume of 153,500 m³. The membrane systems developed by GTT are not self-supporting, the double jacket of the ship's hull forms the actual load-bearing structure for the tanks. The loading tanks are largely adapted to the ship of the ship and integrated into the hull. Two membrane layers referred to as barriers are used to provide leak-proofness and security.

The new CS1 insulation layer is built up of the following four levels (see Figure 3).

- First barrier. The inner impermeable metal membrane forms the actual loading container and is, therefore, in direct contact with the liquefied gas. This first barrier consists of a 0.7 mm thick layer of Invar steel, an alloy having a very low coefficient of thermal expansion.
- Behind this there is an insulating layer of plywood and a 10 cm thickness of polyurethane foam.



- Second barrier. There then follows a thin “Triplex” sheet – a special feature of the CS1 technology because hitherto in membrane tankers the second barrier was also produced from Invar steel. The new panel consists of two outer glass-fibre components and an aluminium layer placed between them. The composite material together with the flexible Triplex strips to be applied later forms the second watertight barrier.

- Between the Triplex panel and the inner metal hull of the ship there is another 20 cm thick layer of expanded polyurethane.

The insulating material composite is adhesively bonded directly to the inside of the double (outer) metal hull of the ship.

Both barriers, but especially the insulation layer of the second barrier, are intended to prevent the extremely cold liquefied gas coming into contact with the steel wall of the ship's hull and causing it to turn brittle due to the very low temperature.

The solution

Surface treatment with atmospheric-pressure plasma is carried out here at the level of the second barrier. The aim is to prepare thousands of flexible Triplex strips for the bonding process. The strips have a width of 30 cm and a total length of approximately 40 km in each tanker. With them the edge seams of the insulating panels measuring 1 m x 3 m are bonded over by means of a two-pack epoxide adhesive to provide complete leak-proofness.

The installation of expensive ventilation and air conditioning systems in the interior of the tanks was one prerequisite for faultless bonding processes but an even more decisive factor was precision pretreatment of the surfaces at the bonding points.

Aker Yards tested various methods but neither chemical processes nor flame treatment of the surfaces delivered the desired success. Only the use of atmospheric-pressure plasma technology developed in Germany fulfilled all of the environmental, safety and efficiency conditions.

Its mode of operation is based on plasma which is also referred to as the "fourth state of matter". This is a material at a high, unstable energy level. Energy is always input via the solid, liquid and gaseous states in the form of heat. But plasma technology does not stop at the gaseous state of matter. If additional energy can put into the material by means of electric discharge the electrons are given higher kinetic energy and leave their atomic shells. Free electrons, ions and molecular fragments are produced. This state, however, can hardly be used at normal pressure because of its instability. Only through the development of a special atmospheric-pressure plasma process were new possibilities of industrial application successfully opened up.

Electrically neutral beam

The systems based on a jet principle operate at atmospheric pressure and with the aid of an electric arc ignited in the jet and the working gas air generate a plasma that flows at zero potential onto the product to be treated. It contains enough excited particles to initiate selective oxidation processes on the surface.

A particular feature is that the emergent beam of plasma is electrically neutral which greatly extends and simplifies its usability. Its intensity is so high that machining speeds of several 100 m/min can be achieved. Typical levels of heating of plastic surfaces during treatment amount here to $\Delta T < 20^\circ\text{C}$. The system also referred to as the "Openair" system is characterised by a threefold action: it activates the surface by selective oxidation processes, discharges the surface at the same time and brings about ultrafine cleaning. The jet systems used can be integrated in-line into a new or already existing production line.

In the process of discharging surfaces this system affords cleaning effects which greatly surpass those of conventional systems. Here the user exploits the high electrostatic discharge effect of a free plasma beam. This effect is further positively affected by the very high speed at which the plasma flows out thereby detaching any adhering particles.

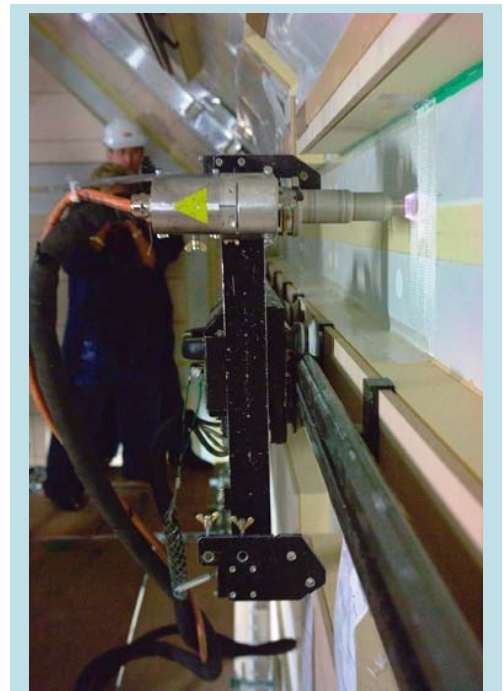


Fig. 4. The pretreatment solution consisted of the first large-area deployment of a rotating jet integrated into the robots. (Photo Yves Guillotin)

Large-area use in a LNG tanker

The pretreatment solution consisted of the first large-area deployment of a rotating jet integrated into the robots and producing plasma without any risk of overheating.

First of all members of staff fixed a three meter long auxiliary rail for the robots in front of the surface to be worked on (see Figure 4). After the start and end points had been programmed the robots controlled the precise operating sequence of the jet and guided it fully automatically at a speed of 6 m/min and at a distance (between jet and surface) of 10 mm over the surface to be treated.

The plasma exerts a twofold action on the Triplex polymer. On the one hand, the microcleaning brings about the destruction of all organic substances on the surface because the plasma beam strikes the surface at a speed of 200 m/s. On the other hand, the treatment activates the surface tension of the treated surface to a value of over 72mN/m. At the end of the operation the auxiliary rail was dismantled and erected afresh at the next area to be treated.

In a second step another team of workers carried out the actual bonding process, i.e. the surface treated with plasma was now bonded over with Triplex strips.

The costs incurred by the shipyard can be estimated from the manpower employed: three hundred workers specially trained for the production of this insulation layer worked in three eight-hour shifts round the clock and in one week produced up to 3.5 km of adhesively bonded strip.

Conclusion

Since its discovery in 1995 atmospheric pressure plasma technology has opened up numerous new applications in industry – in particular in the areas of cleaning, activating and coating. In doing so savings in material and process costs as well as the possibility of obtaining joints in environmentally friendly manner are foreground objectives. Not least this technology owes its worldwide expansion in just a few years to a special feature: the jet systems used are always employed by the user in-line, that is to say directly in the assembly line.

The layer-by-layer removal of organic layers, paint stripping or the partial removal of metallised coatings prior to adhesive bonding, the production of car headlights as well as the treatment of reflectors are just some examples of the successful in-line use of this process.

In the case of bonded joints on aluminium surfaces the plasma achieves reliable joints involving the most varied aluminium alloys and completely replaces costly and ecologically dubious wet chemical processes.

Precision pretreatment of surfaces to be bonded by means of plasma jets also allows the use of modern solvent-free UV adhesives as well as natural systems based on water.

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