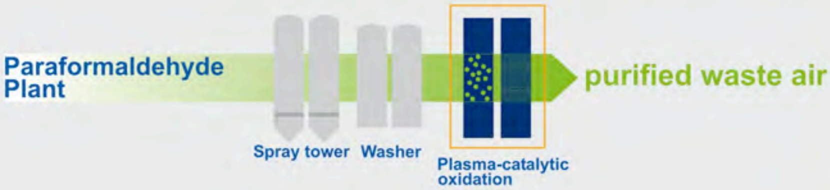
CHEMIE SEIT 1856

INEOS Paraform

GmbH & Co. KG registered office in Mainz/Germany

# LAYMAN REPORT

## Novel waste air treatment unit of the Paraformaldehyde-Plant for the reduction of emissions and smells

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# Introduction

INEOS Paraform GmbH & Co KG is a manufacturer of formaldehyde from which paraformaldehyde (trade name „Granuform“), hexamine and methylal are produced. In Germany INEOS Paraform GmbH & Co KG is the only producer for these chemicals which are sold to many companies in Europe and overseas. The production of paraformaldehyde is of special economic importance since it is an important and indispensable material for the manufacture of many other compounds and goods.
The production of paraformaldehyde generates emissions of formaldehyde, methanol, ammonia and smelling substances. The very large waste air flow of 45000 $m^3$/hour which results from the drying processes contains small traces of these impurities after the passage of washing units. These substances were originally emitted. The limit values for these emissions were lowered with the last amendment of the German Clean Air Act (Technische Anleitung zur Reinhaltung der Luft, abbreviated “TA-Luft”). It was impossible to reach these new limit values with the washing units alone. However, a further reduction by incineration would have required a very large additional energy consumption.

Therefore the aim of our investigations was to develop a process which achieves the required emission reduction with an optimised low consumption of natural gas and hence a minimum CO2-emission in order to make a contribution to the protection of the environment. This request had to be reconciled with the demand for cost effectiveness.

Preliminary tests with differing methods and techniques were made until finally the plasma-supported waste air treatment in combination with a catalytic oxidation was found as the optimal treatment of the exhaust air.

The process was developed with the support of the industrial partners Relox GmbH and Rafflenbeul Anlagenbau GmbH and also by an Institute of the West Pomeranian University of Technology in Szczecin Poland. This process runs at comparatively low temperature and hence low energy demand and delivers the desired result. The process is a novel solution to remove pollutants and strong-smelling substances from the air without creating significant amounts of climate-damaging compounds like nitric oxides or ozone.

In order to implement this new technology at the paraformaldehyde plant an application was placed with the help of the Ministry of the Environment of the State of Rhineland-Palatinate for support by the LIFE+-Program of the European Union. The European Commission acknowledged the innovative character for the advancement of the protection of the environment in Europe. The commission decided to support this technique financially in the frame of the LIFE+-Program.

The aim of this report is to inform the general public and the professional experts alike on the results during the development and the practice of this technology in order to promote its use for new applications.

# Noxious substances from the paraformaldehyde plant

Aqueous formaldehyde solution is concentrated in the paraformaldehyde production plant up to a formaldehyde concentration of approx. 88 %. Then this solution is spray-dried to produce solid paraformaldehyde by removal of water into the air stream. The waste air for the drying steps, altogether 45000 $m^3$/hour, contain formaldehyde, methanol and paraformaldehyde dust which must be removed for pollution control reasons.

In a first step the air stream is purified in washing columns using a dilute aqueous ammonia solution whereby the ammonia reacts with formaldehyde and with the paraformaldehyde dust. Hereby a considerable reduction of the emission is achieved and the recovered substances can be put to use in other applications. The removal of methanol is not quantitative and also traces of formaldehyde and ammonia are emitted. Another effect of this method is the formation of side products which can be smelled in extremely low concentrations without being a hazard source. These side products are not absorbed in the washers due to their very low boiling points.

With the amendment of the German Clean Air Act the requests for the emission limitations of formaldehyde, methanol and ammonia were considerably tightened. The washing process used before the amendment was now no longer capable to comply with the new requirements.

**Figure 1: Paraformaldehyde plant**

# Summary of the research investigations

The noxious substances methanol, ammonia, formaldehyde and the strong-smelling side products are present only in low concentrations and distributed in very large amounts of air which is nearly saturated with water.
The process which should be used for the purification of this air must fulfil the following criteria:

- No generation of further waste air or other waste
- No or only very small generation of secondary emissions
- The costs for purchase, operation and maintenance should be as low as possible.
- The energy consumption should be as low as possible to avoid a large CO2-emission
- In addition, all safety requirements must be complied with which must be observed in the paraformaldehyde plant.
- The operational availability of the plant must be above 90 %.

After comprehensive literature studies and inspection of units in other companies the following possibilities were examined:

- Recirculation and re-use of air
- Reduction of air consumption by modification of the production process
- Improvement of the existing washers
- Upgrading of the washing processes with the addition of different chemicals

- Absorption on activated carbon or zeolites
- Condensation by cooling of the emitted air
- Biological waste air treatment (Bio filter or bio washer)
- Treatment/oxidation with ultraviolet light
- Exposure to ionising air
- Catalytic oxidation alone
- Non-thermal plasma process
- Finally combination of a non-thermal plasma assisted catalytic waste air treatment

Most methods were not practicable for the realisation in the paraformaldehyde plant due to limiting factors. Either the emission reduction was uncertain or the financial implications were not acceptable. Finally the best results were obtained with a combination of a non-thermal plasma generator with a subsequent catalytic treatment unit due to its high degree of heat recovery and hence relatively low energy demand.

## Description of the non-thermal plasma process

The term “non-thermal plasma process” describes a method in which components of the air are activated by the excitation with an electric current. In this process oxygen, nitrogen and water molecules are split into atoms or are converted by electrons into radicals resembling an excitation state like at very high temperatures. Hereof the term “plasma” is derived. This activated state of the atoms causes an enhanced reactivity which can be used for the treatment of noxious substances in the air stream.

The generation of these radicals is achieved in a strong electric field whereby the electrons are constantly produced by discharge processes between two electrodes. The composition of a “plasma module” consists of numerous metal plate electrodes with ceramic plates in between as electric barrier. The air to be ionised is channelled through the gaps of this assembly. A high frequency alternating current in the order up to 12000 Volt and up to 8000 Hertz is applied.

The efficiency of this plasma method for the removal of the noxious substances from the air of the paraformaldehyde production was investigated in-depth by the Westpomeranian Technical University Szczecin/Poland, Faculty of Electrotechnique under the supervision of Dr. Marcel Holub.

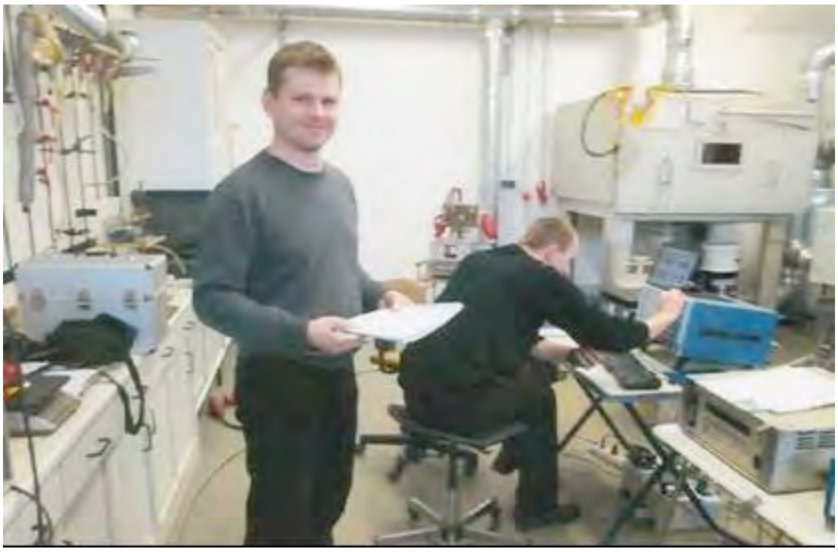

**Figure 2: Dr. Holub / Laboratory of Rafflenbeul Anlagenbau GmbH**

In the evaluation of the degradation rate of the harmful substances in the air stream it is possible to establish a sequence of the efficiency and the degradation rate. Ammonia needs high energy densities and low initial concentrations of around 50 mg/m$^3$ in order to reach the required low end concentrations. At higher initial concentrations and lower energy densities the degradation rate drops. Therefore the non-thermal plasma process is not capable alone to achieve a satisfactory decay of ammonia in the waste air stream since in particular during start-up and finishing processes in the plant increased ammonia values are common.

The oxidation of methanol is achieved much easier with the non-thermal plasma process but not to the extent that one can always do without a subsequent catalyst unit.

The oxidation of formaldehyde is achieved with a high degradation rate. If only formaldehyde would be present in sufficiently low concentrations, then the non-thermal plasma process alone would be acceptable.

It can be stated in summery that the combination of the non- thermal plasma process with the catalytic oxidation process guarantees a better removal of the noxious substances.

It is also known that the performance of the non-thermal plasma process is significant in the oxidation of the smelly substances.

The positive additional influence on the decay of low concentrations of the existing smelling substances was also demonstrated in the trials.

More details on the plasma technology are defined in the new VDI-guideline 2441:2014-03.

# Catalytic combustion of waste air

The first tests for the catalytic treatment of the waste air from the paraformaldehyde plant took place in the laboratory of the company Rafflenbeul Anlagenbau GmbH. Airstreams were loaded under defined conditions with ammonia or methanol, heated and then passed over catalytic materials. In these tests the air velocity, the temperature of the catalyst and the amount of substances in the air were varied.

At first a pellet catalyst with a nickel/copper ingredient was used. Good decay rates could be achieved in the temperature range of 230-250 °C. If the air was loaded with a substance quantity exceeding 1 %, an exothermic reaction became noticeable. These laboratory tests finally led to the construction of a small pilot plant which was directly connected to the off-gas from the paraformaldehyde plant.

**Figure 3: Test equipment in the research laboratory Rafflenbeul**


**Figure 4: Pilot unit at the paraformaldehyde plant**

The result from the laboratory tests led to the construction of a pilot plant which was operated in the side stream of a waste air stream from the plant. Thus the laboratory results could be verified under production conditions. Besides the decay rate other parameters like contamination and abrasion of the catalyst were studied.

If paraformaldehyde dust gets unto the catalytic surface formation of soot is likely to occur. It is the task of the plasma unit to oxidise these deposits on the catalyst and to keep the catalytic surface clean and activated.
These studies proved, however, that the pellet catalyst shows abrasion and is not stable over a long time span. The alternative found was a honey-comb catalyst with a coating of platinum. This type of catalyst requires a different design of the waste air treatment unit which also has the advantage of a high heat recovery.

This minimises the energy costs and reduces the carbon dioxide emission. The mechanical stability of the honey-comb catalyst, its low flow resistance and the higher heat recovery finally led to the decision to switch to this catalyst although a somewhat higher process temperature is needed for the activation of the catalytic activity of the platinum.

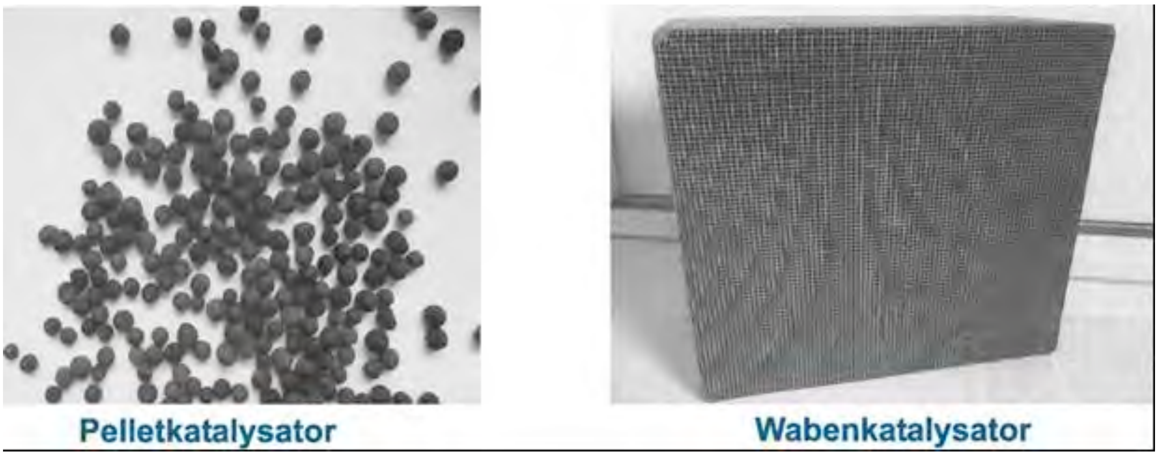


**Figure 5: Pellet catalyst Honey-comb catalyst**

The heat recovery is achieved with ceramic tiles which are heated up at first by the outflowing hot off-gas, then, after flow reversal of the gas, the ceramic mass releases the heat unto the cold inflowing gas. In this way a heat recovery of over 90 % can be achieved. Only the remaining heat loss must be replaced by heating with an earth gas burner. An uninterruptible operating mode needs three identical chambers which are involved in the catalytic oxidation and also in the heat recovery. The calculations showed that in these three chambers 30 tons of ceramic tiles are necessary in order to achieve a high heat recovery, storage and transfer. With this design the requirements for a high heat recovery and correspondingly low energy consumption could be fulfilled.
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# Design of the combination process

The optimal decay rates of the noxious substances are achieved with a combination of the non- thermal plasma process and the catalytic post-treatment of the waste air from the plant.
The realisation of the industrial unit for the treatment of the total waste air flow of 45000 m$^3$ is shown in the following scheme:

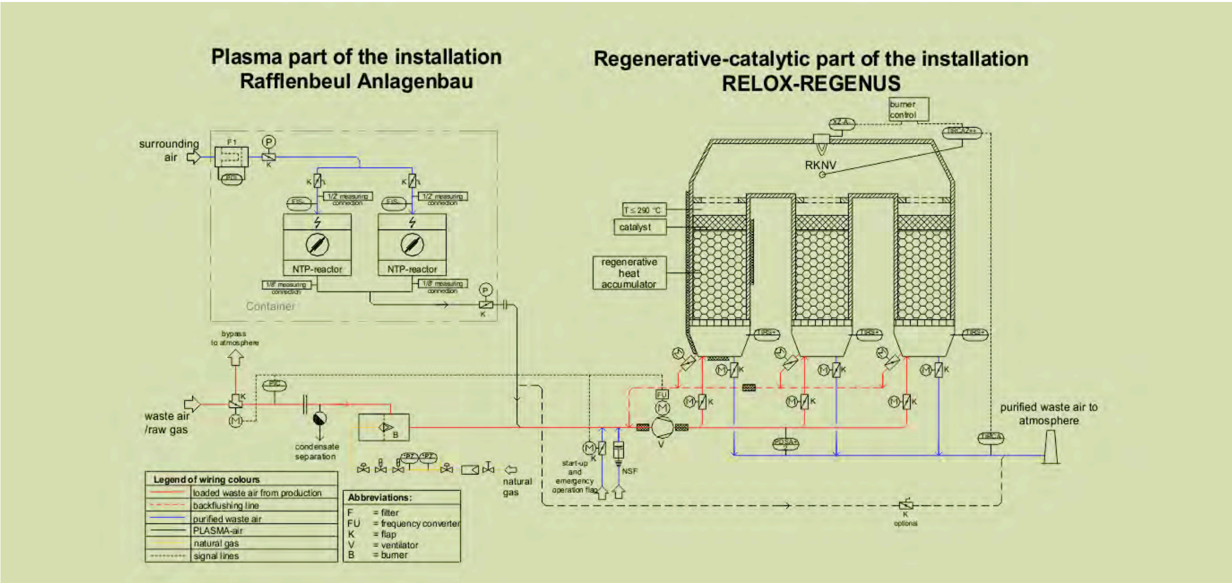


**Figure 6: Process flow chart of the combined plasma and catalytic waste air treatment plant**

The plasma unit blows in activated air into the off-gas from the plant. Then the combined air reaches the catalytic section while being heated with an earth gas burner. Three reaction chambers are installed in the catalytic section in order to avoid slippage of untreated air and hence avoid an uncontrolled emission.

While the ceramic mass in one chamber is heated up by the hot off-air, the hot ceramic mass in another chamber is used to heat up the cold inflowing air. The air flow is varied in quick change between these chambers which is achieved with large instrument air-pressure operated disc valves.  Since the plasma unit destroys already some of the noxious components in the air, the operating temperature can be lowered thus saving energy.

Initially it was necessary for the technical installation of the plant to install the required infrastructure. One important precondition was the upgrading of the electric power supply of the paraformaldehyde plant by installing a 20 KV-transformer, an upgrading of the low voltage distribution net, installation of an earth gas supply by pipe to the location of the waste air treatment unit and the construction of a concrete foundation as well as a chimney for the off-air.

The contractors were company Rafflenbeul Anlagenbau GmbH for the plasma-catalytic part and the company Relox/ Bremerhaven for the catalytic part.

**Figure 7: Picture of the waste air treatment unit with control room, enclosure of the plasma unit and air blower**

# Investigation of the waste air

The analytic measurement methods for the quantitative determination of the noxious substances in the air are described in legal regulations and specifications.
A defined amount of air is sucked through three series-connected washing bottles using a calibrated measuring gas pump. The substances are washed out from the air and transferred into the water. The noxious substances should be absorbed in the first two washing bottles while the third bottle should not contain any chemicals as proof that all had been absorbed before.

Wash bottle equipment with calibrated measuring gas pump

Determination of ammonia by titration

**Figure 8: Sample drawing and analytical determination**

The aqueous solution of the first two bottles is united and the amount of noxious substance determined using the following analytical methods:

- Determination of formaldehyde using a photometric method
- Determination of ammonia by titration with acid
- Determination of methanol by gas chromatography

The test for nitric oxides is carried out directly in the off-gas stream using calibrated measurement devices of the same type like in private heating installations.
The investigation on the presence of ozone is carried out using standardised diagnostic dipsticks.

Smelling substances are controlled using a standardised olfactometric procedure. Under defined conditions different persons give a judgement on their smell perception in comparison to standardised air samples.

# Results

Formaldehyde is removed to a very high degree. Small traces of methanol can still be detected. The degree of oxidation is around 90 %.

Ammonia is firstly optimised by the dosage regulation of the washing columns. After the oxidative waste air purification the measurement values are below the legal limit value of 30 mg/m³.

The compliance to the German Clean Air Act for the substances formaldehyde, methanol and ammonia is achieved and the results are often considerably lower than the limit values.

The energy efficiency of the unit is calculated from the following data: The waste air from the plant has a mean temperature of 27 °C. After treatment the air leaves the unit with a mean temperature of 66 °C. The temperature difference of 39 °C is equivalent to the heat which cannot be recovered. The catalyst has a mean temperature of 291 °C. The degree of heat recuperation as calculated from these data amounts to 91 %. Only 9 % of the inserted heat energy is lost and must be provided for anew by the earth gas heating.

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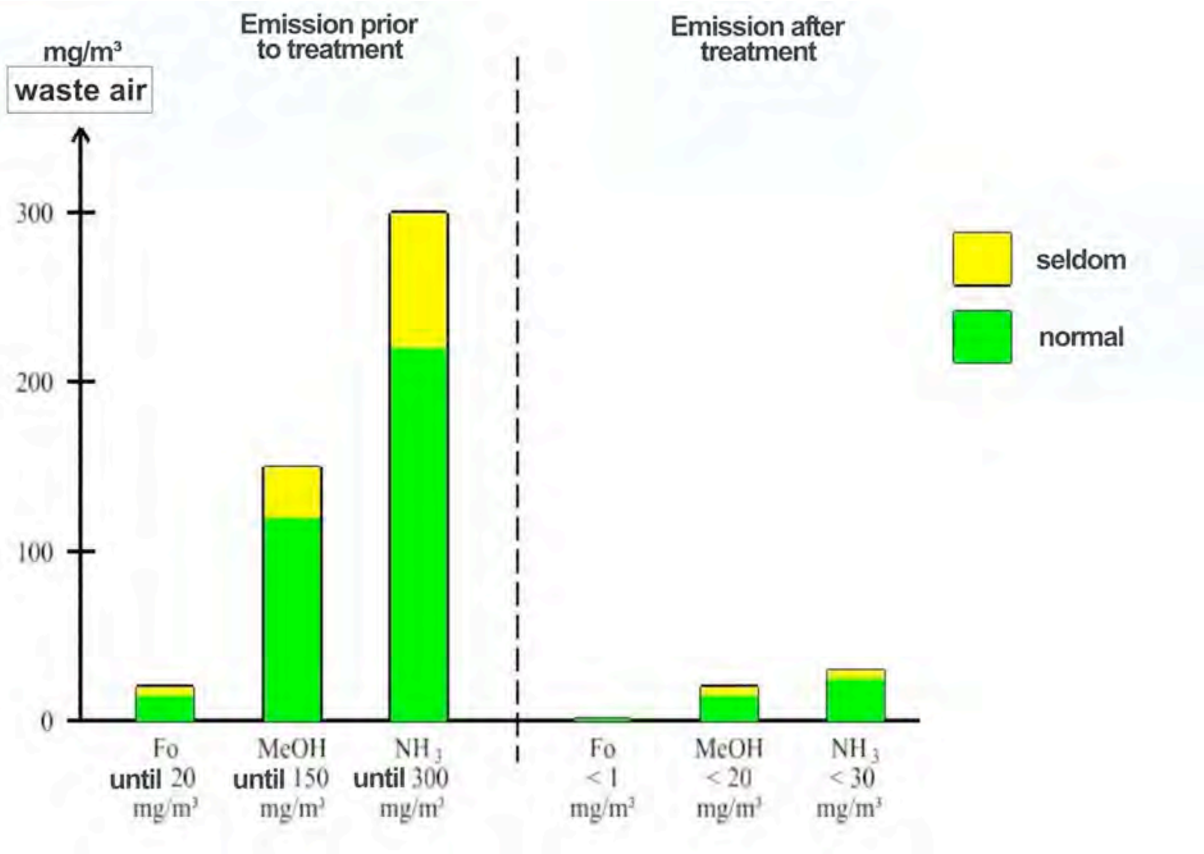


**Figure 9: Results oft he waste air treatment**

# Evaluation of the project

By combining two different techniques a new standard for the limitation of emissions in plants for the manufacture of paraformaldehyde has been created.
It is assumed that this combination technology will find further fields of application in the long term.

The realisation was achieved under adherence to the financial frame conditions and within the estimated time. The very good analytic results of this prototype of a new technology justify the promotion by the European Union under the LIFE+-Program.

INEOS Paraform has undertaken a considerable financial risk with the investment into this novel prototype technology. In the final analysis this outstanding result became possible by the trust into the skill of the employees of the company as well as of the participating component suppliers and last but not least by the scientific research on the European level, here by the University of Szczecin in Poland.

# Awards

Award certificate from the Ökoprofit Initiative of the City of Mainz

The City of Mainz promotes the engagement of companies in its administrative area for the aims of the environmental conservation. In 2014, INEOS Paraform GmbH & Co KG was awarded with an award certificate for its engagement for clean air in Mainz and its participation in the Ökoprofit initiative.

## Umweltpreis (Environmental Prize) of the Federal State Rhineland Palatinate


Award certificate of the City of Main


Environmental prize Rhineland Palatinate

**Figure 10: Certificates**

The Ministry for the Environment, Agriculture, Food, Viniculture and Forestry of the federal state Rhineland Palatinate in the person of Mrs. Ulrike Höfken awarded the Environmental Prize 2014 to INEOS Paraform GmbH & Co KG because of the uniqueness in Europe of the project “Innovative waste air treatment unit of the paraformaldehyde plant “ and its role model for other companies and production installations.

# Acknowledgements

INEOS Paraform GmbH & Co KG wants to thank all participants who worked for the realisation of this waste air treatment project in the paraformaldehyde plant and for the support of the European Union in the frame of the LIFE+-Program for the promotion of improvements to the environment. Hereunto are included the permit authorities of the City of Mainz, the component suppliers and subcontractors, the staff of the scientific institute of the University Szczecin/Poland, the ladies and gentlemen of the European commission and also of the monitoring team of Astrale GEIE-Particip GmbH. Without their support the realisation of this environmental project who have been hardly possible.

The Project was conducted under the following title:
EU-LIFE+ Umweltprojekt Nr. 11/DE/1073
Duration of Promotion: July 1st, 2012 until March 31st, 2015
The amount of promotion covered 25 % of the total costs.
Project website: www.granuform-projekt.de
Film in Youtube of the inauguration of the waste air treatment unit by Mrs. Eveline Lemke, Minister of Economics RLP: www.youtube.com/watch?v=1C4Z4XRXiic

CHEMIE SEIT 1856

INEOS Paraform GmbH & Co. KG

Hauptstrasse 30 - D 55120 Mainz Germany
Contact person: Dipl. – Ing. Ralf Timimi
Telephone 0049-6131-118
E-mail: ralf.timimi@ineos.com

Link:
Further information under
www.granuform-projekt.de