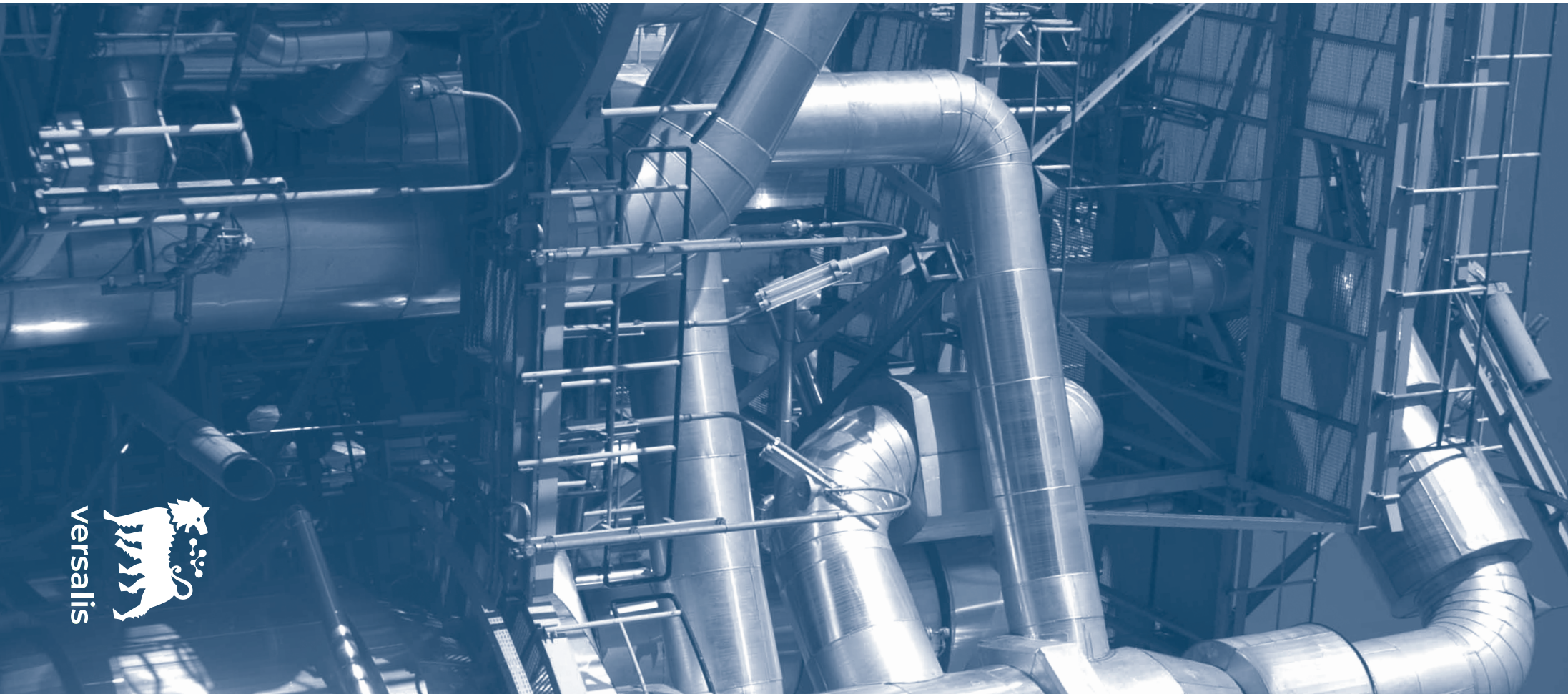
SAN

Styrene Acrylonitrile copolymers

CONTINUOUS MASS POLYMERIZATION TECHNOLOGY



versalis

Versalis proprietary process technologies available for licensing

Our company

Versalis - the petrochemical subsidiary of Eni - is a dynamic player in its industry sector facing the multifold market needs through different skills.

With a history as European manufacturer with more than 50 years of operating experience, Versalis stands as a complete, reliable and now global supplier in the basic chemicals, intermediates, plastics and elastomers market with a widespread sales network.

Relying on continuous development in its production plants as well as in its products, strengthening the management of the knowledge gained through its long industrial experience, Versalis has become a worldwide licensor of its proprietary technologies and proprietary catalysts. The strong integration between R&D, Technology and Engineering departments, as well as a deep market expertise, are the key strengths for finding answers to customers requirements.

Our commitment to excellence, in quality of our products and services, makes our company an active partner for the growth of customers involved in petrochemical business.

Through engineering services, technical assistance, marketing support and continuous innovation, our knowledge is the key strength to customize any new project throughout all phases.

Customers can rely on this strong service-oriented outlook and benefit from a product portfolio that strikes a perfect balance of processability and mechanical properties, performance and eco-friendliness.

Introduction to Versalis SAN continuous mass technology

Versalis has been producing Styrene-Acrylonitrile resin via traditional suspension process since the 60s. In the early 90s, Versalis started the production of SAN based on an innovative continuous mass technology developed meanwhile by its R&D and already extensively used for GPPS and HIPS since the 70s. In 1993 the production and sales of suspension based products were completely stopped and Versalis decided to concentrate only on continuous mass technology.

The key features of Versalis SAN continuous mass technology are:

- high transparency, rigidity and hardness. High chemical resistance, dimensional stability, colour brilliance as well as low content of residual monomers;
- minimum amounts and number of chemicals introduced in the process;
- fine-tuned macromolecular structure (molecular weight and its distribution);
- flexible technology allowing tailor-made solutions for specific needs, in terms of plant capacity and products range;
- really simple process scheme and easy process control;
- low environmental impact with respect to the suspension technology (no water used in the process, limited amount of vents containing VOC are generated by the process);
- special and unique process and mechanical design of key equipment such as the reactor and devolatilizer.

After a complete switch from suspension to continuous mass process, Versalis is in the position to offer a complete and well balanced Kostil® product portfolio, a benchmark within the European scenario.

Versalis can always provide appropriate solutions to different client's needs thanks to its capabilities and experience in the following fields:

Research & development

The presence of a strong R&D team, established in Mantova since the early 70s, qualifies Versalis as an outstanding owner of know-how in the field of styrenics. Reliable and updated facilities (pilot plants, synthesis and analytical labs, equipment for polymer processing), allow Versalis to continuously improve the technology in order to support the styrenics business in a competitive and demanding market scenario. Additional services are then available for potential Licensees, such as technical assistance, training, development of analytical methods, site assistance for start-up and follow up, development of tailor made products on demand.

Process design & operational experience

Process design is flexible and able to face different conditions and constraints.
Any project is individually evaluated to offer the best solution, tailored to specific customers needs.
Thermal and fluodynamic analysis (CFD) are extensively applied to the design of key equipment such as reactors, agitators and devolatilizers.
The design takes also advantage of the Versalis long-term manufacturing experience.
New technological solutions are first tested in production plants; then the acquired experience is transferred to the licensed technology, in order to ensure not only the best process performances, but also a safe and reliable plant arrangement.

Mechanical design

Versalis Engineering Dept. has always been working in close coordination with the Process Dept. This fact has allowed to develop unique and well sound engineering solutions for critical equipment, that guarantee the best results in terms of mechanical reliability and process performances.

The flexibility of Versalis SAN continuous mass technology allows to provide with a single line convenient solution for a broad range of economically feasible capacities: up to 80 kt/y. The plant arrangement can be tuned to fit required targets, such as special grades and/or peculiar products range.

Wastes and emissions

The main liquid organic wastes and vents are sent to a thermal oxidizer in order to comply with the most severe European and international standard for minimization of the environmental impact.

Industrial applications

A Versalis SAN unit, based on proprietary technology, is on-stream in Italy (50 kt/y, since 1993).

Main process parameters

	per MT SAN
Raw Materials	1,010 - 1,015 kg
Electricity	0.18 MWh
Fuel Gas (10,000 kcal/kg)	20 - 25 kg
Steam	130 kg

The KOSTIL® SAN product portfolio

Versalis SAN products are characterized by a very good balance between key properties such as:

- high transparency, rigidity and hardness;
- high chemical resistance, dimensional stability, colour brilliance;
- very low residual monomer content;
- low amounts of chemical consumption for the same property balance.

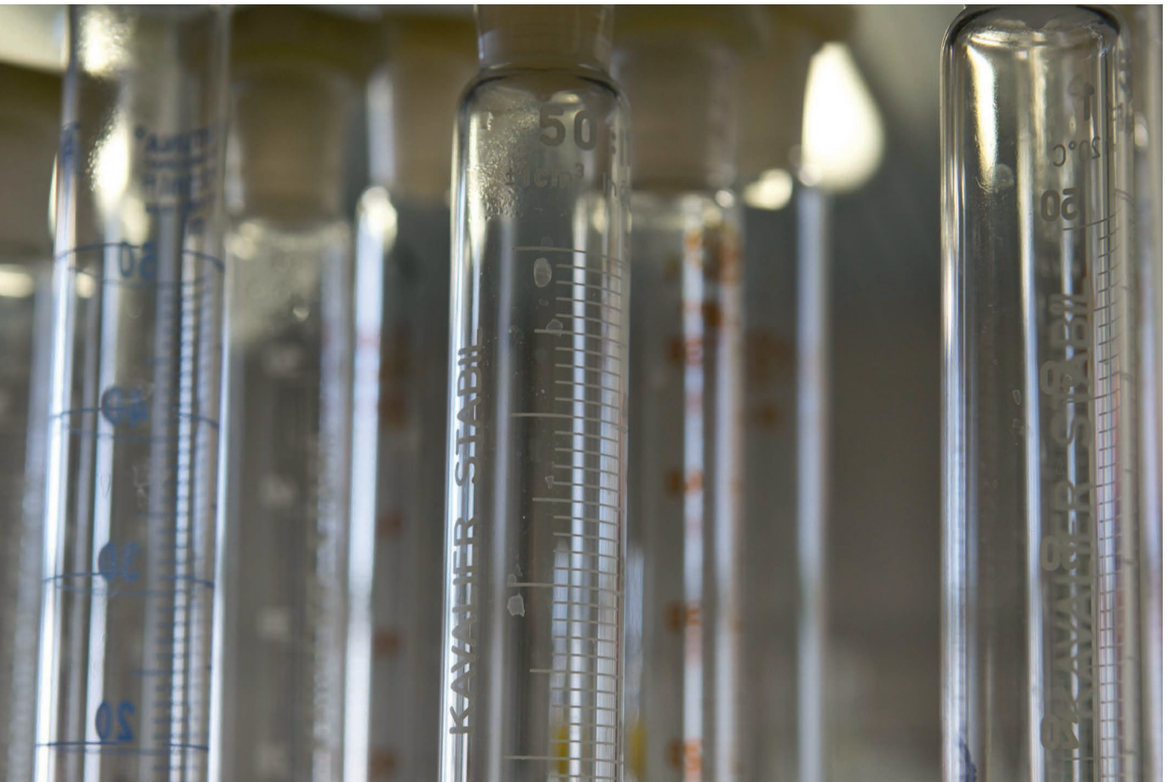
This set of characteristics allows the Kostil® products portfolio to cover the following fields of application.

Injection moulding

- Households and small appliances. Refrigerators clear components.
- Cosmetic packaging.
- Medical and pharmaceutical items. Copier, printer and fax components.

Extrusion

- Lighting, bathroom furnishing.
- Blow moulding.
- Bottles and containers.



Process description

From suspension to continuous mass process

The suspension SAN grades have been used for decades as main ingredients for the ABS production. At the end of the 80s, the search for cleaner ABS grades has pushed Versalis R&D to introduce SAN intermediates with superior colour transparency and improved stability. At the same time, higher polymer transparency of the grades used for direct injection moulding applications (low coloured, glass clear types) was strongly required by the market.
Last but not least, the environmental issues have become in last decades more and more important and unavoidable in relation to the quality of the finished product (monomers and residual substances) and production features (quantity and quality of effluents, emissions in the workplace, etc.).

The continuous mass production process does not use any raw materials or additives other than those used in the reaction (i.e. no water is needed in the reaction section) and thus allows a drastic reduction in the number and quantity of emissions. The simplified continuous mass SAN process scheme consists basically of a closed loop, single step technology.
Raw materials are continuously fed and polymerized in the reaction section. The non reacted monomers/solvent are separated from the polymer in the devolatilization section, condensed and recycled back to the reaction. The molten polymer is finally pelletized and sent to storage.

Only a minimum amount of organic liquid purge discharge is necessary to remove impurities that can not be polymerized and non-polymerizable matters that otherwise would tend to accumulate.
The Versalis SAN technology is based on a continuous mass polymerization of styrene and acrylonitrile. Both monomers are first fed to a purification section, before being mixed with chemicals in a mixing section.
The mass reaction is carried out in the presence of solvent.
The mixture is then fed to the polymerization section, generally composed by two/three plug flow reactors in series.
The whole reaction section arrangement is selected case by case, in order to meet specific requirements.
At the end of the reaction train, the polymer solution is sent to a devolatilization section, consisting of two stages operated in series and under vacuum conditions.

The monomers and low boiling compounds are removed from the polymer, which is finally sent to the pelletizing unit.
Some additives are continuously fed and mixed to the polymer before pelletizing. The heat for process needs is provided by a thermal oil system. The vapour mixture, after condensation, is continuously recycled to the mixing section.
Non condensed vapours/inert gases from the vacuum system and liquid organic purge from the condensation section are sent to a thermal oxidizer.

Process design advanced features

Versalis SAN technology is characterized by the following proprietary advanced design features:

Polymerization section

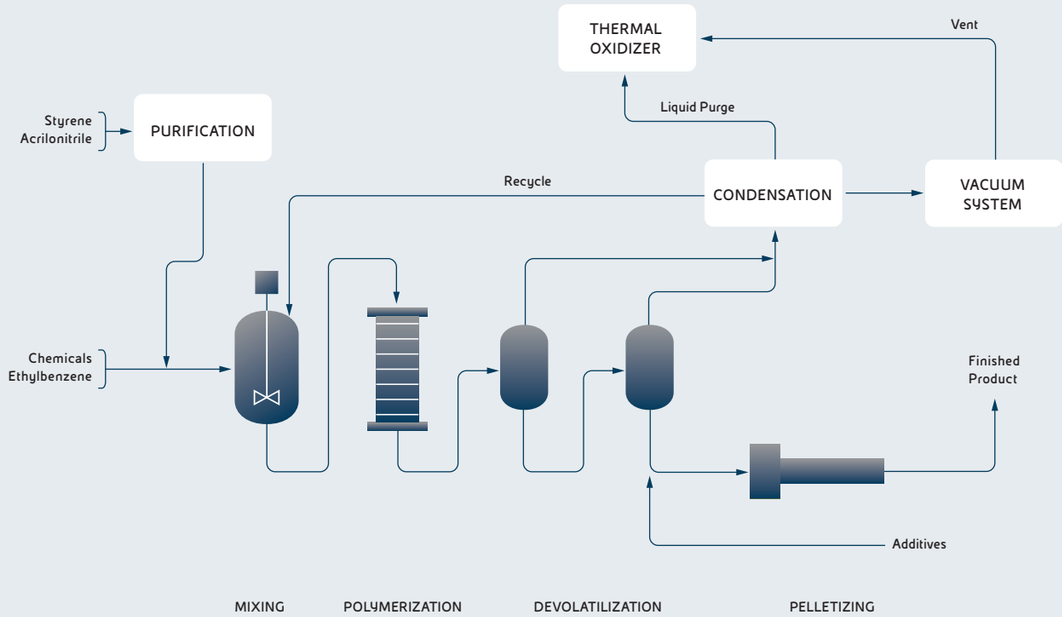
The main items are full plug-flow reactors (PFRs); thanks to agitation and a high specific thermal exchange surface area, they are characterized by very precise control of the thermal reaction profile.
No need of shut down for cleaning or washing with solvent is necessary to remove contaminations (present with other types of reactors). Any specific need in terms of product quality/portfolio can be matched by tuning the reaction train arrangement.

Devolatilization section

This involves two-stage operation, with high heat and mass transfer rates and very low residence times.
This combination of factors leads to a very efficient monomer and organic matter removal even at relatively low temperature (thus minimizing polymer chain degradation) and without the addition of water or other stripping agents.

Fig. 1

SAN continuous mass • process scheme



Proprietary process technologies portfolio

Biotech

PROESA® 2G Ethanol and Cellulosic Sugars

Phenol and derivatives

Cumene (with PBE-1 zeolite based proprietary catalyst)*
Phenol, Acetone, Alphamethylstyrene*
High selectivity Cyclohexanone
Acetone hydrogenation to Isopropyl Alcohol*
Isopropyl Alcohol to Cumene**
Ammoximation (with Titanium silicalite based proprietary catalyst TS-1)

DMC and derivatives

Dimethylcarbonate (via Carbon Monoxide and Methanol)*
Diphenylcarbonate*

Proprietary catalysts

Titanium silicalite
PBE-1 Zeolite
PBE-2 Zeolite

Styrenics

Ethylbenzene (with PBE-1 and PBE-2 zeolite based proprietary catalyst)
Styrene
GPPS
HIPS
EPS suspension polymerization
ABS continuous mass polymerization
SAN

Polyethylene

LDPE
EVA

Elastomers

Emulsion-SBR
HSL Latices
Solution-SBR
TPR
LCBR
HCBR
NBR
Carboxylated latices
EP(D)M

* Co-licensing in cooperation with Lummus Technology (a McDermott International Company).
** Close to commercialization.

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Responsible Care

SINCERT

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