Proprietary process technology

NBR

Nitrile Butadiene Rubber copolymers

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 NBR technology

NBR butadiene-acrylonitrile rubbers are copolymers of butadiene (BD) and acrylonitrile (AN) produced by means of an emulsion polymerisation reaction initiated by redox catalyst systems.
The high oil and fuel resistance over a wide temperature range is certainly one of the most important feature of Nitrile Rubber. Furthermore, goods NBR-based are well addressed for their high strength and resistance to abrasion properties. Versalis NBR process is an advanced emulsion technology based on continuous radicalic polymerization of butadiene and acrylonitrile. In absence of other specific operations, the AN distribution along the macromolecules should be irregular; proprietary technology crosses over this problem by feeding monomers along the reaction train; in this way, in each reactor, the AN/BD ratio is ideal to achieve the right monomers' statistical distribution. Versalis technology includes a plant section devoted to the pre-treatment of the waste water able to significantly reduce the pollutants content before the discharge into to the Central Waste Water Treatment sewer system.

Key features of Versalis NBR production technology are:

- high flexibility in terms of product mix and good quality constancy and reproducibility;
- monomers and modifier's feeding are individually defined per each grade and each rate, increasing the flexibility of the process and the control of comonomers' distribution in the macromoleculas;
- possibility to carry over the NBR Plant accepting a wide range of monomer purity, with no lack of product quality;
- no downtime is required to change the grade in reaction;
- very low quantity of reject material sent to incineration (high recycle of process water and unreacted monomers);
- low environmental impact due to section devoted to the pre-treatment of the waste water
- low concentration of the residual VOC content in the exhaust (no thermal oxidation is required).

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 Ravenna since the early 70s, qualifies Versalis as an outstanding owner of know-how in the field of elastomers. Reliable and updated facilities (pilot plants, synthesis and analytical labs, equipment for elastomer processing), allow Versalis to continuously up-to-date the technology in order to support the elastomers business in a very 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) can be applied to the design of key equipment such as reactors and agitators. The design takes also advantage of the Versalis long-term manufacturing experience. New technological solutions are first tested in production plants and the acquired experience transferred to the licensed technology, in order to reach not only the best process performances, but also a safe and reliable plant arrangement.

Mechanical design

Versalis Engineering Dept. has been working in close coordination with the Process Dept. since a long time. 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.

Versalis NBR technology allows to provide with a single line a fairly broad range of economically feasible capacities up to 33 kt/y per reaction unit.

Wastes and emissions

The design of the plant is carried out taking into account the target of the minimization of the effluents, as this means more efficiency and lower environmental impact. The process produces waste water which are pre-treated ISBL by means of a filtration/concentration process to remove large part of the pollutants before being discharged to a standard bio-treatment. Continuous process vents are sent to the treatment system (OSBL). Large waste air emission from finishing lines requires only a scrubbing (dedusting) due to its low concentration of pollutants. Solid waste material, during normal operation, is limited to small amounts of filtering elements, plastic cans used as chemicals' package and rubber cleanings from paved areas.

Industrial applications

An NBR production plant (33 kt/y) is on stream at the Versalis site in Porto Torres (Italy). This plant was first built up in 1973 as a swing line eSBR / NBR. In 1985 the plant was converted to NBR production only and in 1990 underwent a general process optimization.

Main process parameters

	per MT of NBR
Raw Materials (Butadiene + Acrylonitrile)	1,035 kg
Electricity	0.75 MWh
Steam	3.2 MT

Data are referred to 1 MT of NBR product, assuming 99.5% acrylonitrile and 99.5% 1,2 butadiene purities.

The AN/BD ratio in NBR varies widely, depending on the required final properties. The following Table shows how the AN level influences the NBR properties:

Low AN content	Property	High AN content
↓	Processability	↑
↓	Cure rate with S curing system	↑
↓	Oil, fuel resistance	↑
↓	Compatibility with polar polymers	↑
↓	Low air & gas permeability	↑
↓	Tensile strength	↑
↓	Abrasion	↑
↓	Heat ageing	↑
↑	Cure rate with peroxides	↓
↑	Compression set	↓
↑	Resilience	↓
↑	Hysteresis	↓
↑	Low temperature flexibility	↓

The product portfolio allowed by Versalis technology is based on five levels of acrylonitrile content in Versalis NBR polymers: low (19%), medium-low (28%), medium high (33%), high (39%) and very high (45%), thus allowing to give the widest properties to the products.

The Europrene® NBR portfolio

The Versalis NBR technology is able to manufacture many grades of polymers through a cold emulsion polymerization process. Changing the polymer composition (% of AN) and viscosity is possible to obtain products characterized by:

- good processability;
- good oil resistance;
- high mechanical properties.

The main applications of Versalis NBR grades are:

- gasket, seals, O-ring;
- hoses, belts, cables, printing rolls;
- molded and extruded products;
- latex applications, adhesives.

Process description

The term emulsion polymerization is used to describe a reaction in which the monomers are emulsified in a medium (water) with the aid of emulsifying agents. The monomers are present almost entirely as emulsion droplets dispersed in a continuous phase. A free radical chain mechanism is accepted to explain the polymerization which consists of three phases: initiation (production of free radicals by means of a redox system), chain propagation and termination. Redox system consists of a reductant and an oxidant which react together with the generation of a free radical which initiates polymerization of the monomers. The soap also plays a part in influencing reaction rate.
Chain propagation is thus initiated and can continue until all the monomer available is reacted. It is necessary to control the chain length to produce the optimum polymer properties. Chain length is controlled by the addition of a chain transfer agent or modifier.

Temperature control is important during chain propagation as high temperatures favour undesirable side reactions.
Cross linking will also occur if the polymerization is allowed to proceed to completion and it is therefore necessary to stop the reaction short of completion so that optimum properties can be obtained. To achieve this, the reaction is terminated at the desired monomer conversion by the addition of shortstopping chemicals. Versalis NBR process is continuous technology, based on isothermal "cold" radicalic polymerization of butadiene and acrylonitrile.

The base NBR Plant is composed by one Reaction and Monomer Recovery line and a single Finishing line. After BDE caustic washing (to remove polymerization inhibitors) demi water, monomers, redox system, emulsifying system and modifier are premixed and precooled (to control the reaction starting temperature).

Polymerization takes place in the first stirred reactor of the train and, as the reaction is exothermic, each reactor is equipped with a coil where boiling ammonia is fed to remove the reaction heat to keep constant temperature along the reaction train.
Modifier and monomers can be added to some reactors of the train in order to obtain better monomer distribution in the polymer chain (monomer effect) and better control of the molecular weight (modifier effect).

After reaction has reached the required monomers conversion, short stopper is added and the emulsion is sent to the Monomer Recovery Section in order to recover the unreacted monomers.
Latex is stored, blended and sent to the Finishing Line where it is coagulated in small crumbs that are washed and fed to the mechanical dewatering and the thermal dryer. The dried product is then baled, wrapped and packed.

Specific sections are included ISBL the base plant, such as the ammonia refrigerating unit and the waste water pre-treatment (filtration + concentration of the finishing water, steam stripping of the process water).

Process design advanced features

Versalis proprietary technology has been developed with a great attention to the properties of the polymer in terms of randomness and mechanical properties.

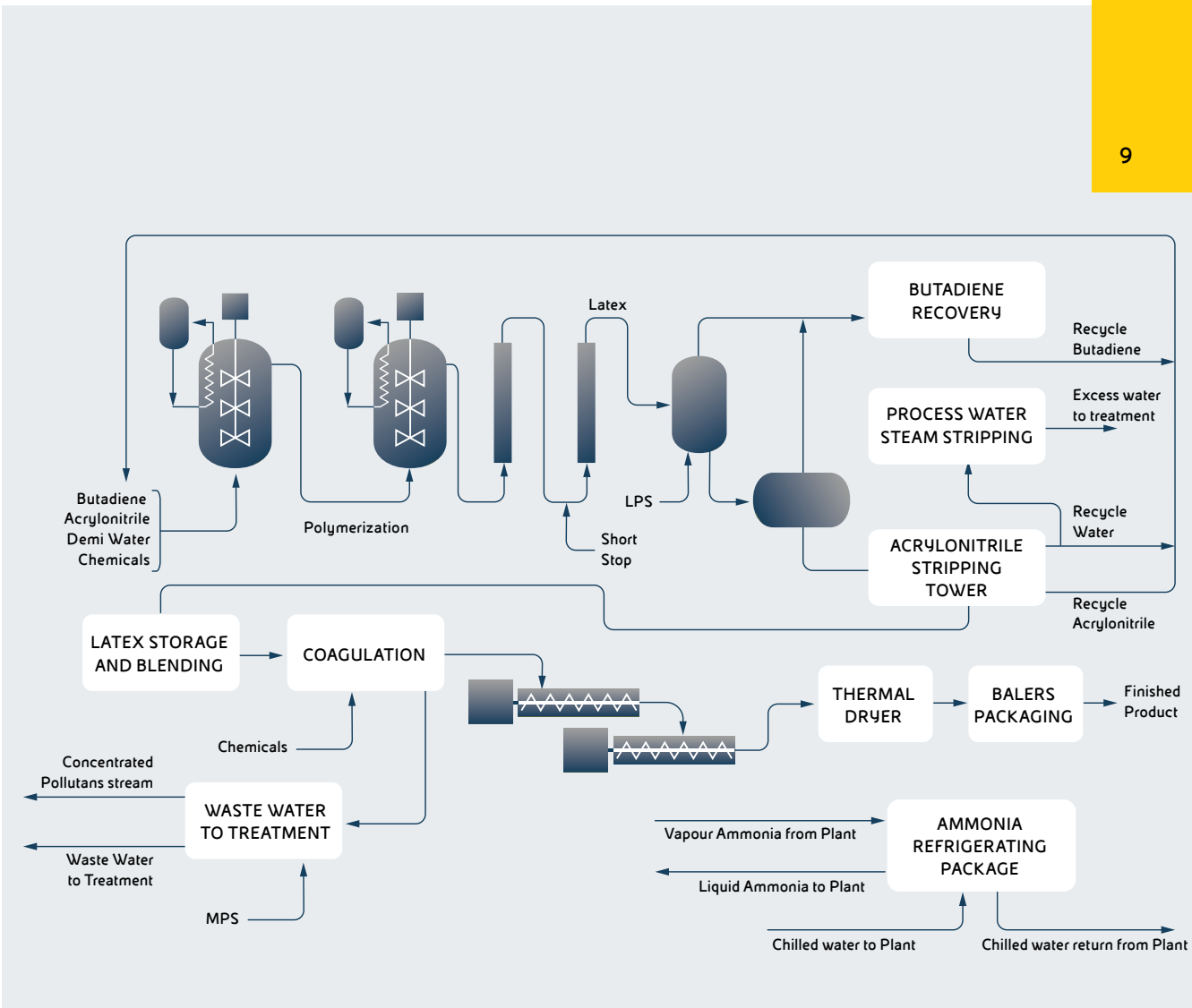
The Versalis portfolio is wide and covers quite all the applications of the "cold" NBR grades. To reach this result, our technology takes into great account the temperature control of the reaction train (which in turn leads to a closer control of polymer microstructure), the quality of the chemicals used in the process and the environmental issues of its technology.

The competitiveness of our proprietary technology is based on the following main key-points:

- high reacting volume per reactor, thus allowing higher plant capacity with same number of reactors;
- monomers can be fed along the reaction train; in this way, in each reactor, the AN/BD ratio is ideal to achieve the right monomers' statistical distribution;
- possibility to carry over the NBR Plant accepting a wide range of monomer purity, with no lack of product quality;
- great reduction of COD and Suspended Solid in the waste water stream sent to Waste water treatment;
- low concentration of the residual VOC content in the exhaust (no thermal oxidation is required).

fig. 1

NBR • 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

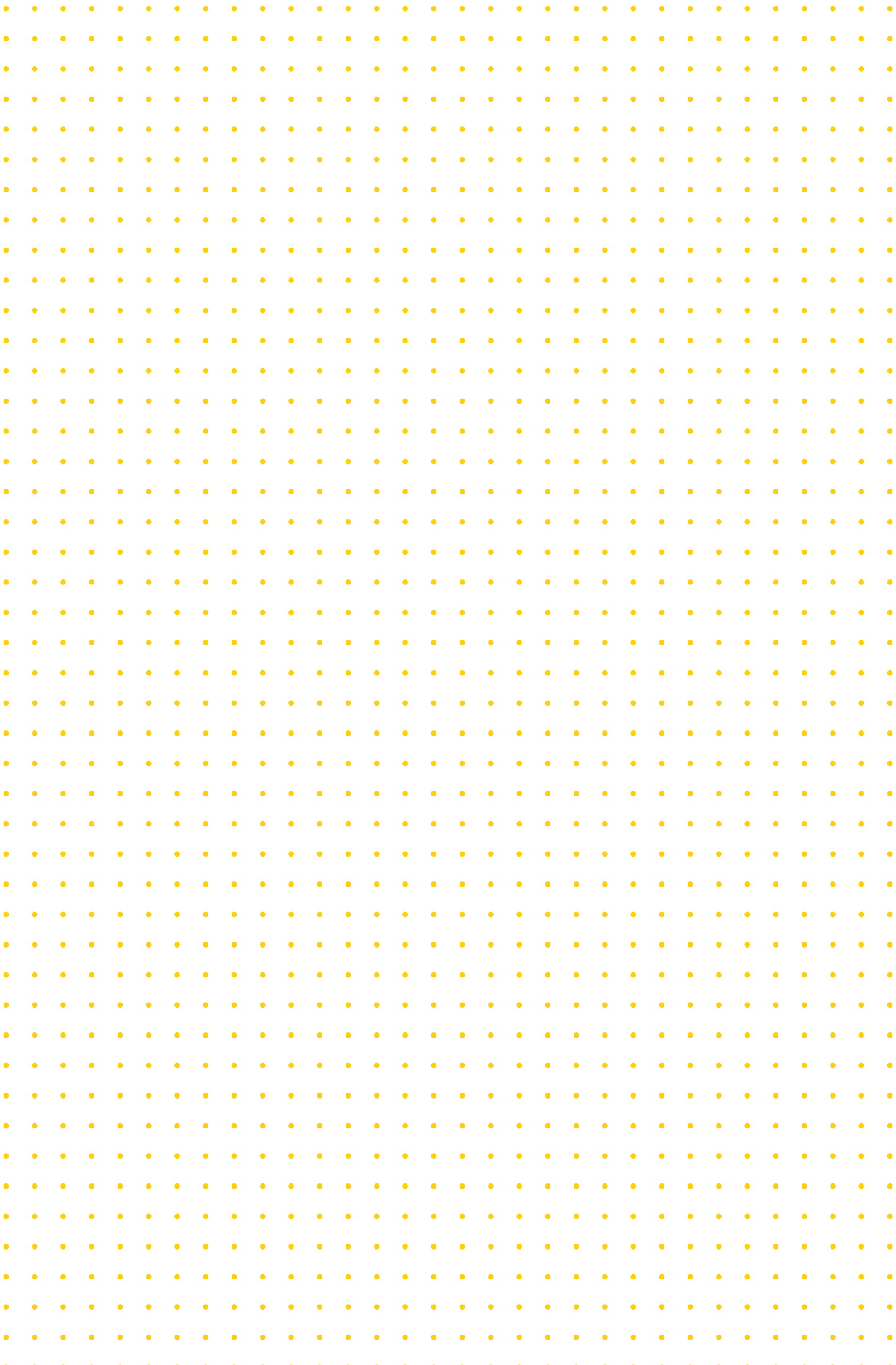
Polyethylene

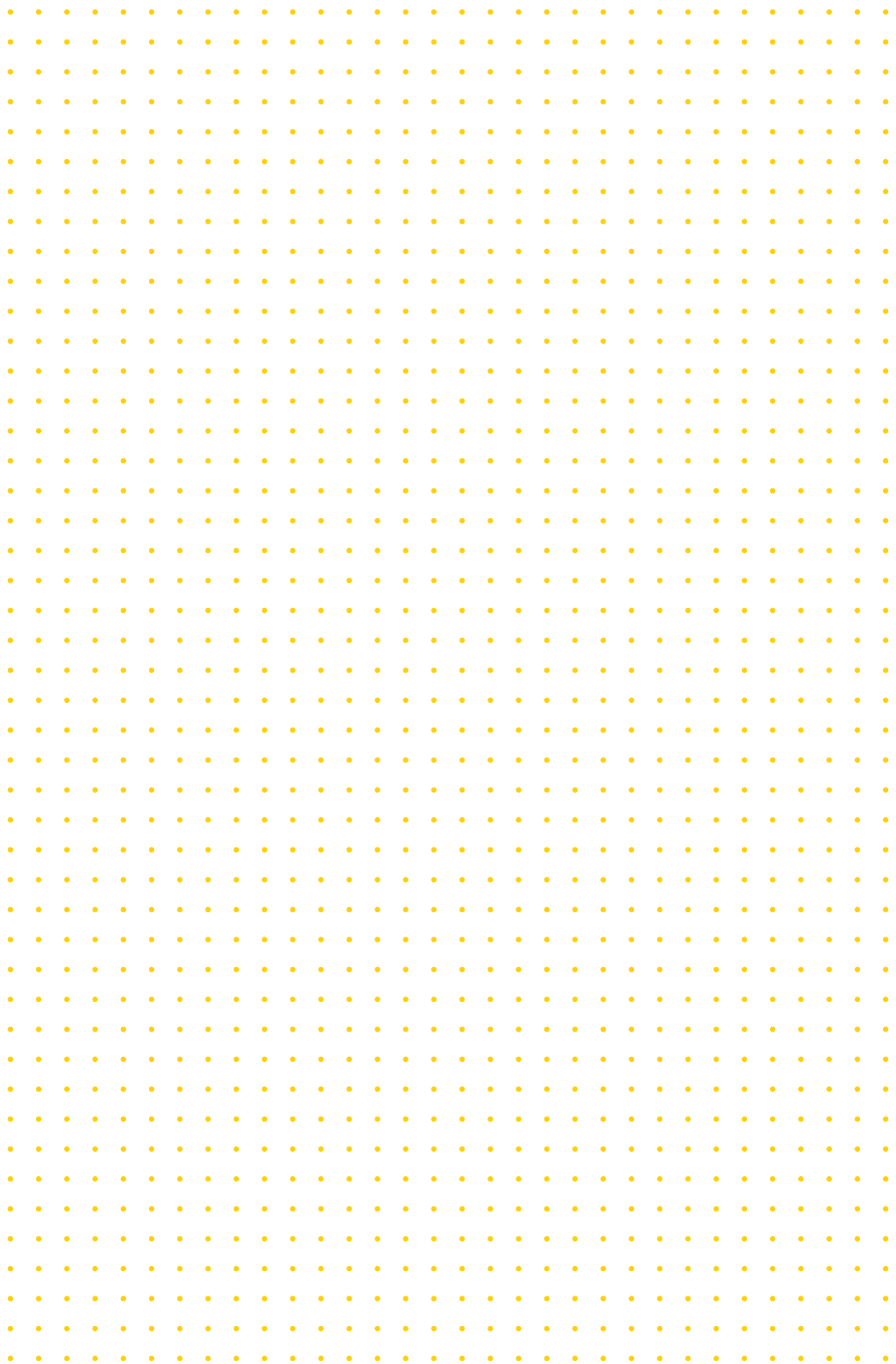
LDPE
EVA

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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