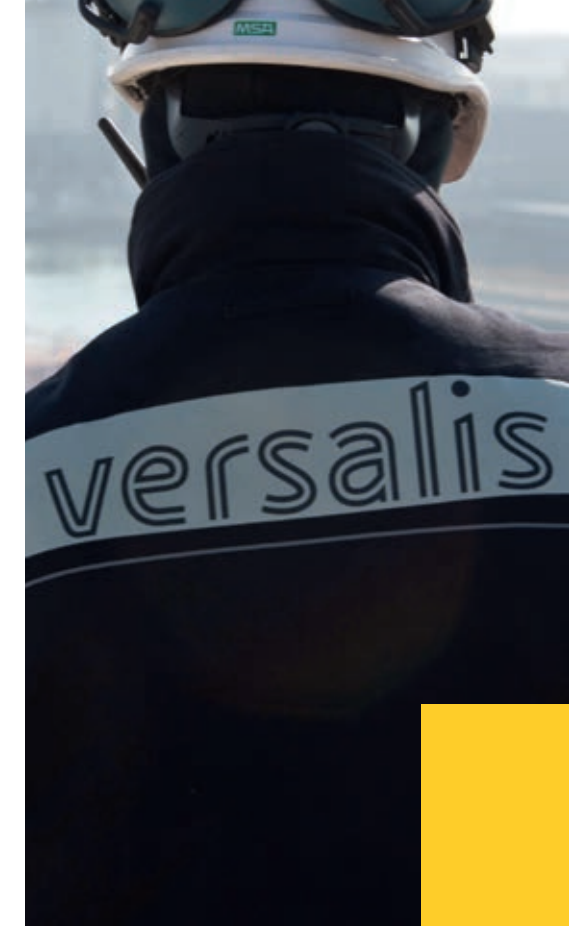


Proprietary process technology

CYCLOHEXANONE OXIME

AMMOXINATION OF CYCLOHEXANONE WITH TITANIUM SILICATE (TS-1) PROPRIETARY CATALYST





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 Cyclohexanone Oxime process

Versalis is in the position to offer the most advanced process and technology to produce Cyclohexanone Oxime, the key intermediate for the production of Caprolactam and then of Nylon 6. The process is based on the reaction of cyclohexanone and ammonia in presence of dilute hydrogen peroxide as oxidizing agent (so-called ammoximation reaction) and uses proprietary Titanium Silicalite catalyst (TS-1), a high performances composite material specifically designed for industrial oxidation reactions. The ammoximation process is a straightforward one-step oxime production process wherein no hydroxylamine formation step is required and no ammonium sulphate is co-produced.

Main features of the innovative Versalis Cyclohexanone Oxime process are:

- lower capital expenditure due to the elimination of the hydroxylamine formation step;
- elimination of the ammonium sulphate formation, still one heavy drawback in the traditional technologies;
- unrivalled level of plant safety due to the very mild reaction conditions and proprietary reactor design;
- unique selectivity to Cyclohexanone Oxime in the reaction stage, what it keeps easier the purification stages and lower the raw material and utilities consumption;
- higher plant reliability and stability, as well as stable cyclohexanone oxime quality over time, coupled with the high catalyst lifetime which makes the catalyst cost negligible on the total cost of production;
- low environmental impact due to elimination of the ammonia burning step necessary for hydroxylamine production.

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

Research and operation

Versalis background and expertise comes from manufacturing experience and constant lab & pilot plant testing. Since the early stages of development, our Cyclohexanone Oxime proprietary process technology has gained benefit from a deep cooperation between leading scientists in the TS-1 catalyst field and technicians involved in industrial production at Versalis (former EniChem).

Process design

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 fluidynamic analysis (CFD) are extensively applied to the design of key equipment such as ammoximation reactor, its feed distributors, agitator and filtering system.

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.

Titanium Silicalite (TS-1) proprietary catalyst

Titanium Silicalite (TS-1) catalyst, one of the most important innovation in heterogeneous catalysis over the last decades, is a high performances composite material specifically designed for industrial oxidation reactions with hydrogen peroxide. TS-1 is the result of long-term research within eni group associated with direct Versalis' experience in industrial oxidation reactions.

The unique performances of the catalyst are due to the specific features of isolated Ti active sites, able to efficiently promote activity and selectivity in oxidation reactions with hydrogen peroxide.

Wastes and emissions

The process produces very small amount of wastes; waste water has low salt content; oil drains are low and discontinues. Solid wastes consist in small quantity of spent catalyst to be washed with demineralised water and dumped at an adequate location. Vent-gas from the units are sent to a proper waste gas treatment sections in order to lower all the plant emissions to a practically negligible amount.

Industrial applications

A demonstration plant (12 KTA capacity) was built at Versalis' Porto Marghera site (former EniChem) and started up in 1994.

The technology is now fully proven at industrial scale, with a 70 KTA capacity unit on stream since 2001 and a 100 KTA capacity unit on stream since 2014, whose produced cyclohexanone oxime has been feeding since then to downstream Caprolactam units.

Product quality

Cyclohexanone Oxime (dry basis)	99.8% wt typical
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Main process parameters

Material Balance	MT per MT Cy-one Oxime
Cyclohexanone (as 100%)	0.875
Ammonia (as 100%)	0.165
Hydrogen Peroxide (as 100%)	0.345

Utilities Consumption	MT per MT Cy-one Oxime
Low pressure steam consumption	2.5

Process description

Cyclohexanone, ammonia and hydrogen peroxide are fed to the reactor where the ammoximation reaction takes place in presence of Titanium Silicalite (TS-1) proprietary catalyst and tertiary-butanol (TBA) as solvent.

The reaction takes place in liquid phase and is exothermic (some of the reaction heat is recovered to heat up reagents).

The catalyst acts by form of solid microspheres dispersed in the reaction media. The reactor is a refrigerated continuous stirred tank reactor (CSTR reactor type) equipped with filters that allow the liquid reaction product to leave the reactor and retains the solid catalyst inside.

A discontinuous make-up of fresh catalyst takes place from the catalyst feed unit and an amount of spent catalyst is purged from the bottom of the reactor, in a definite volume of slurry. Gas vent coming from the ammoximation reactor is sent to a washing column and then to a dedicated catalytic treatment section.

The liquid reactor effluent consists mainly of oxime, tertiary-butanol, water, unconverted cyclohexanone and ammonia. The liquid reactor effluent is sent to the TBA recovery column where TBA and ammonia are recovered as top product and recycled back to the reactor.

The raw oxime product coming from the bottom of the TBA recovery column is sent to a liquid-liquid oxime extraction column where toluene is used as extracting

agent to recover anhydrous raw oxime. Waste water, with traces of toluene and oxime coming out from the bottom of the oxime extraction column, is sent to a toluene stripping column where organic compounds are recovered from water.

Waste water is then sent to an oxidative treatment section where residual organics are oxidised in presence of hydrogen peroxide. Anhydrous raw oxime with toluene is sent to oxime/toluene distillation column.

Toluene is recovered as top product of the oxime/toluene distillation column and is recycled back to the oxime extraction column. A small portion of the recycle toluene is sent to the toluene purification column in order to purge out some minor by-products. Raw anhydrous oxime is recovered as bottom product from oxime/toluene distillation column and is sent to the cyclohexanone recovery column where pure oxime is recovered as bottom product while unconverted cyclohexanone is recycled back to the reactor.

Process is provided with an adequate vent gas treatment section in order to lower all the plant emission to a practically negligible amount.

Process is also provided with a specific system of on-line analyzers and safety interlocks which provide, together with proprietary design of the reactors and unique performances of the TS-1 catalyst, an unrivalled level of plant safety and reliability.

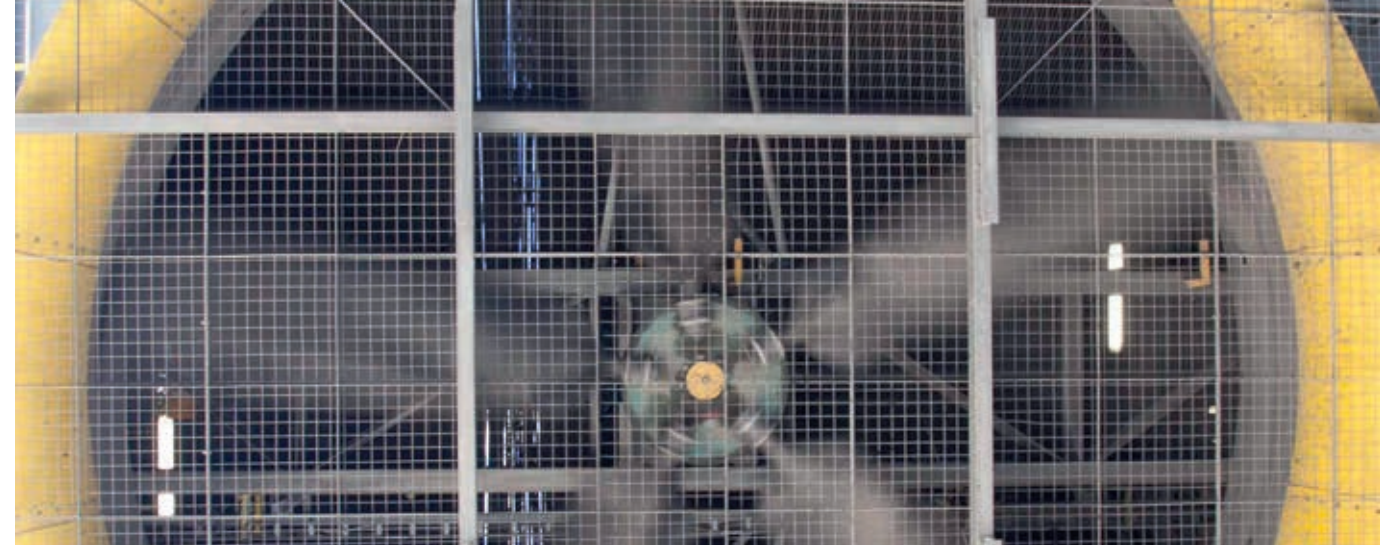
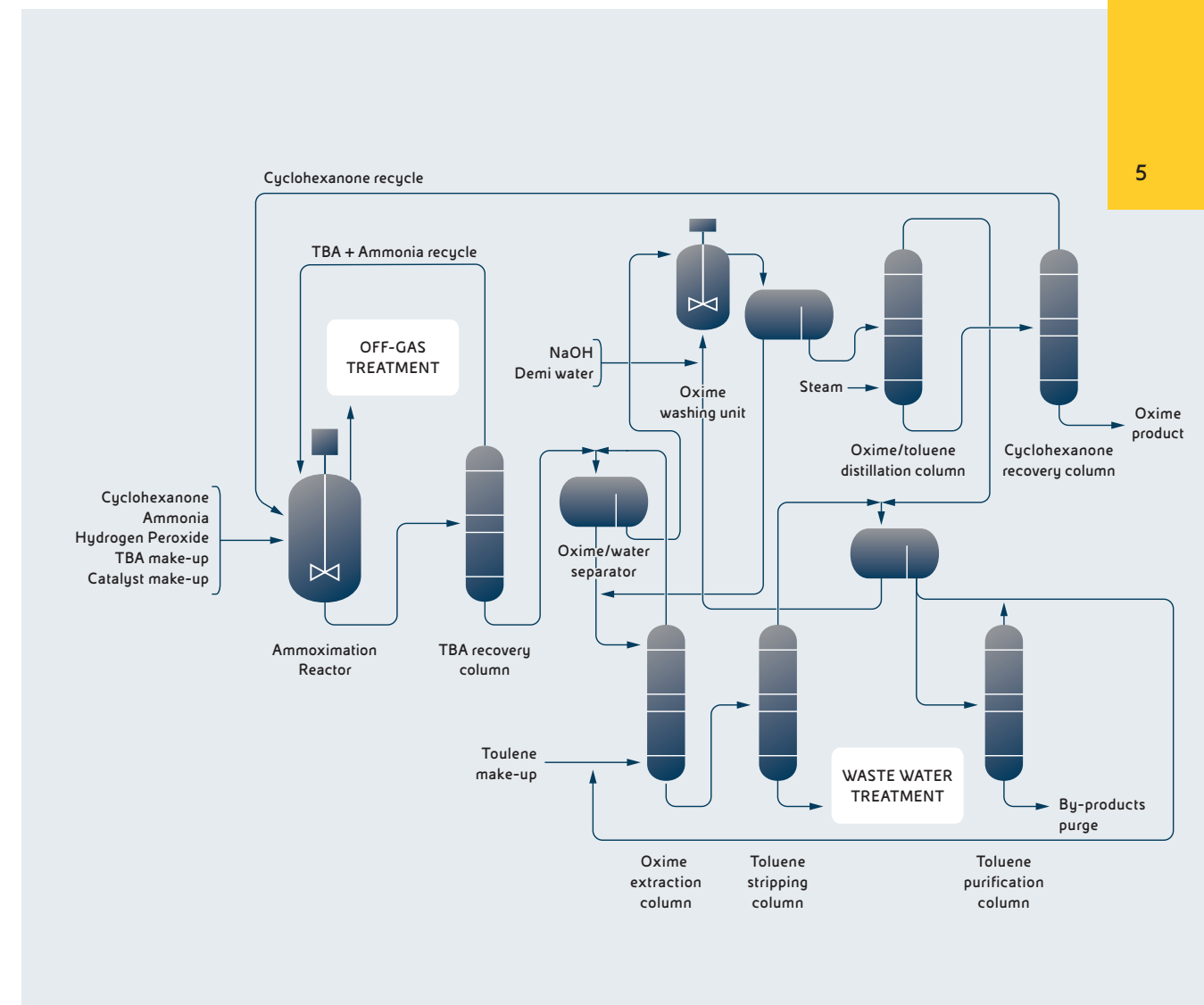


fig.1



Proprietary process technologies portfolio

Biotech

PROESA® 2G Ethanol and Cellulosic Sugars
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Phenol and derivatives

Cumene (with PBE-1 zeolite based proprietary catalyst)*
Phenol, Acetone, Alkylphenols*
High selectivity Cyclohexanone
Acetone hydrogenation to Isopropyl Alcohol*
Isopropyl Alcohol to Cumene**
Ammoxidation (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

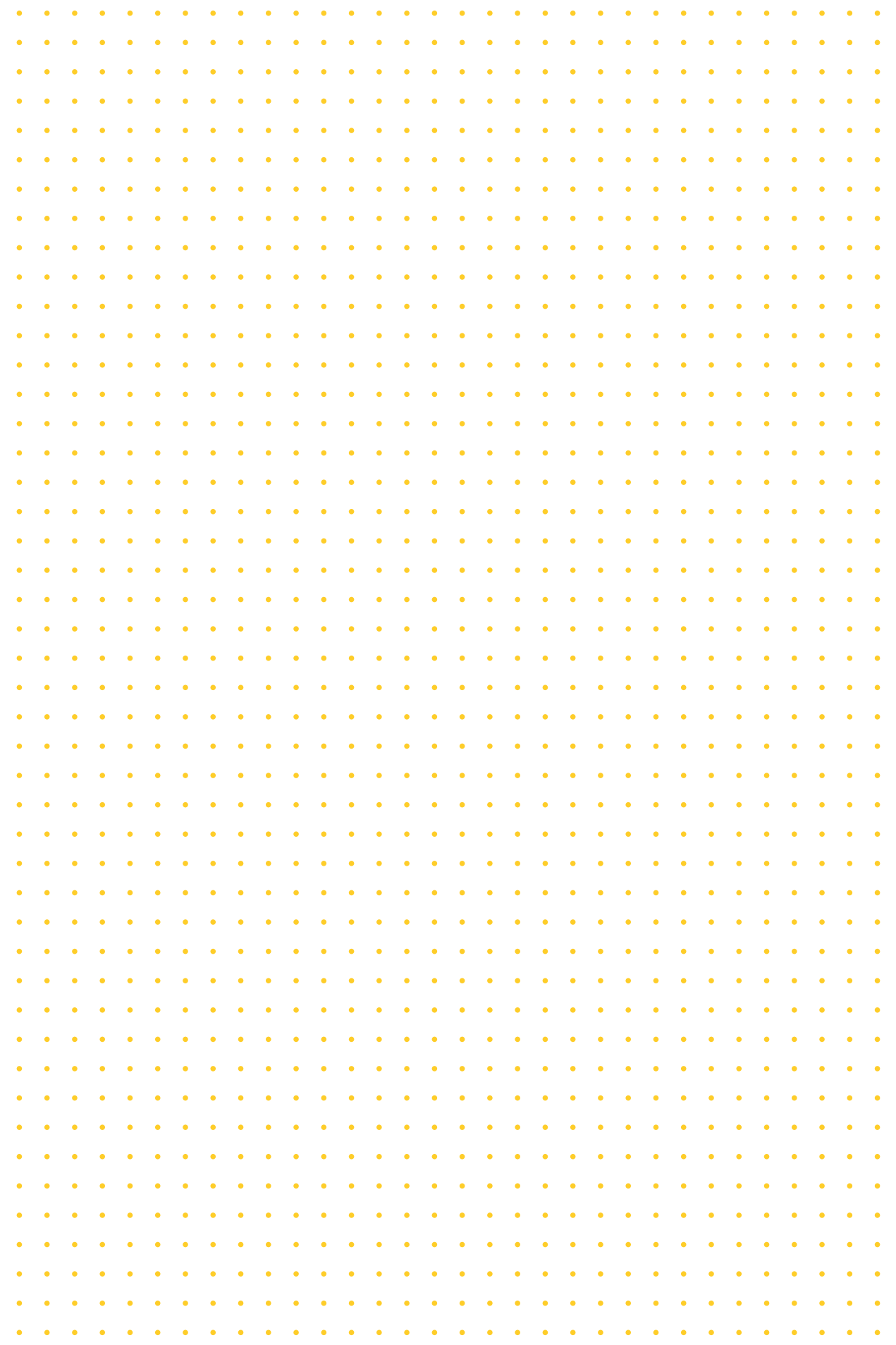
Ethylbenzene (with PBE-1 and PBE-2 zeolite based proprietary catalyst)
Styrene
GPPS
HIPS
EPS suspension polymerization
ABS continuous mass polymerization
SAN

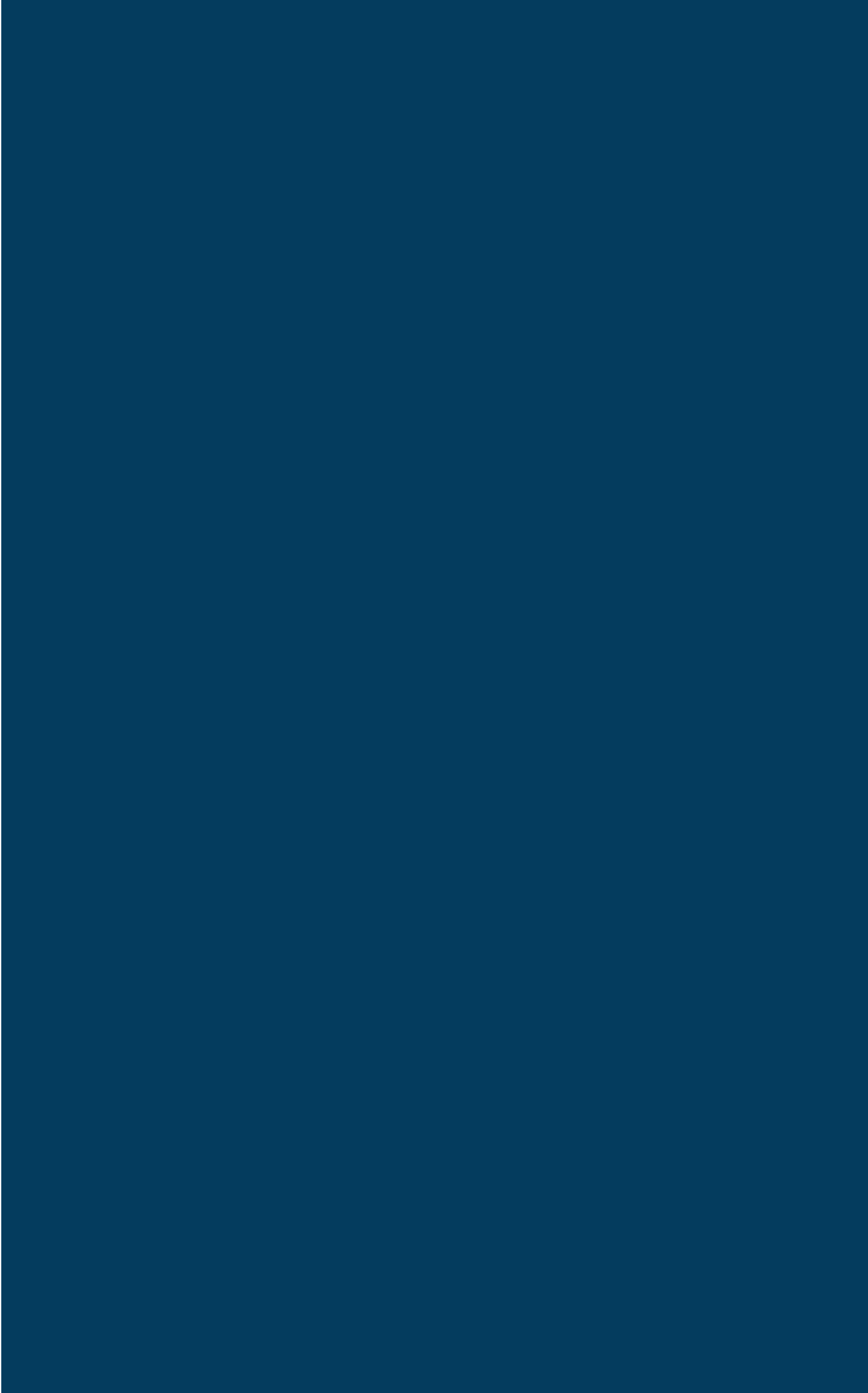
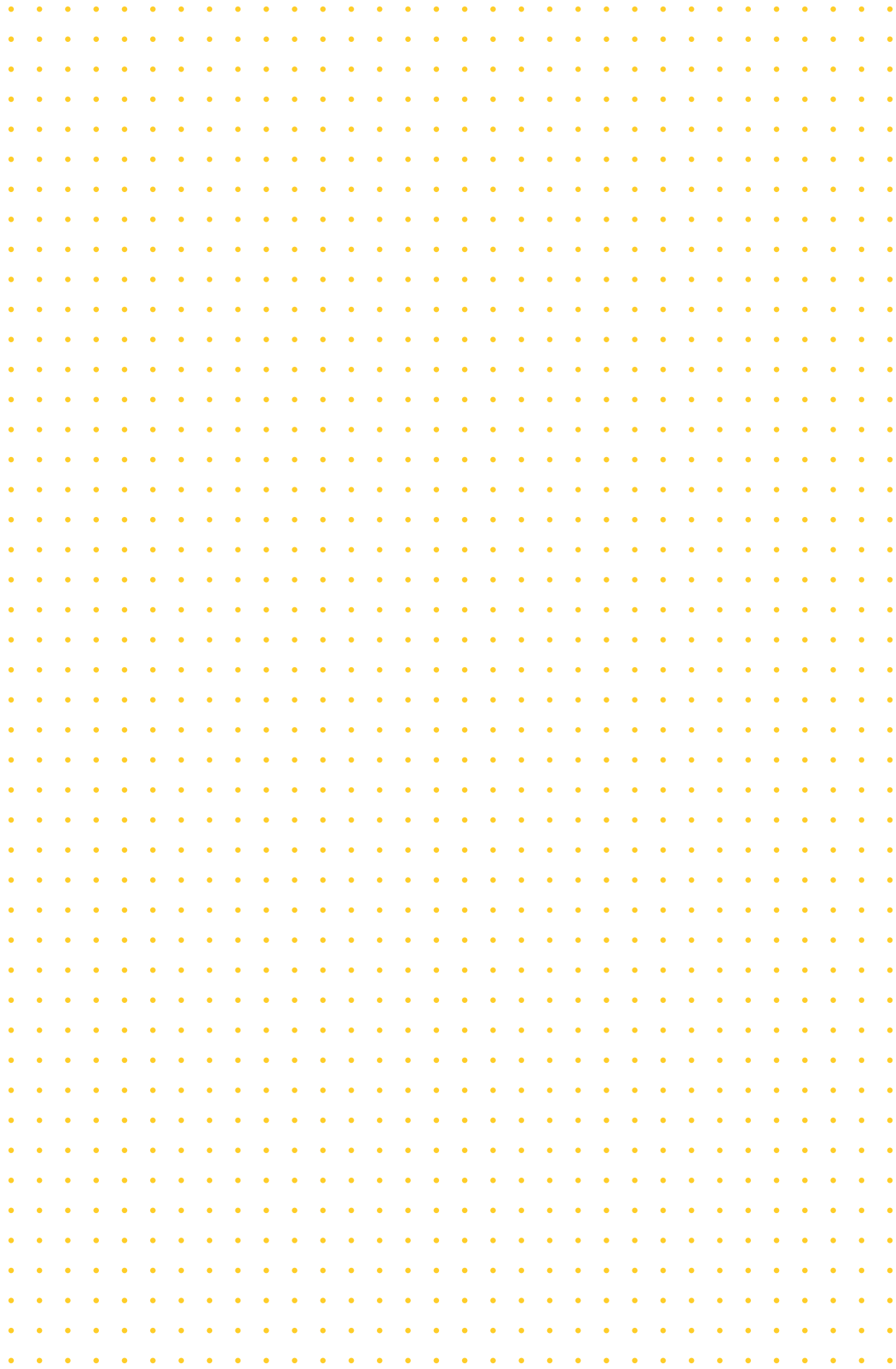
Polyethylene

LDPE
EVA

Elastomers

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







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11 - 2018