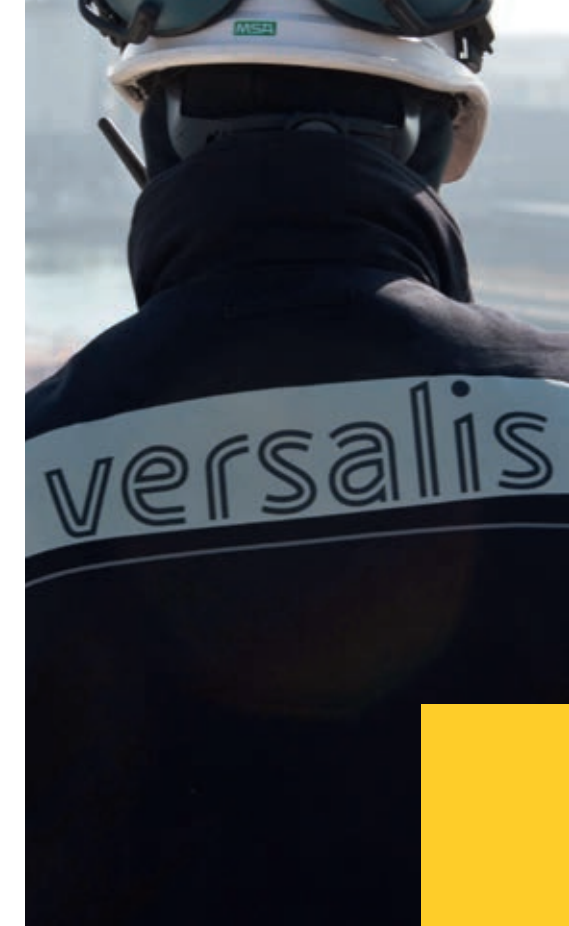


Proprietary process technology

PHENOL & ACETONE





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 Phenol & acetone technology

The Versalis phenol process has been developed since 70s and internally applied to increase plant capacities and improve product quality. New unit operations have been designed and implemented (phenol extractive distillation) and new techniques applied (reaction CFD modelling) since then, leading today to a very competitive phenol Technology that gives outstanding performances in the market. Since 2007 Versalis and Lummus Technology, offer the Versalis/Lummus Technology for the production of phenol. This technology incorporates many decades of operating and design experience by Versalis with Lummus design expertise, as well as its proven and superior technology features.

Main features of Versalis/Lummus phenol technology are:

- proprietary intrinsically safe low-medium pressure oxidation reactors (designed to enhance selectivity to CHP and to minimize reactor volume);
- proprietary cleavage reactors with very low CHP hold up (designed to ensure low selectivity to impurities);
- high phenol and acetone purity, suitable for bisphenol A - polycarbonate grade applications;
- very low raw material consumption without tar cracking;
- very low CHP hold up in concentration section;
- innovative extractive distillation of phenol with very low steam consumption;
- operating experience of a more than 40 years phenol producer is made available to be transferred with proper training to licensees;
- available proven design option for AMS by product: hydrogenate AMS back to cumene or refine AMS for sale.

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 in phenol production technology comes from manufacturing experience and constant lab & pilot plant testing. A great and updated know how comes from continuous lab & pilot plant testing on reactors and distillation section to be then applied on phenol industrial plants.

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 fluidodynamic analysis (CFD) are extensively applied to the design of key equipment such as reactors, their internals and main heat exchangers.

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.

Wastes and emissions

The process produces liquid wastes as process water with organics and salts (pre-treated ISBL in order to be sent to a standard bio-treatment OSBL) and heavy organics that can be sent to a power station or to an incinerator as fuel.

The plant emissions are mainly from the cumene oxidation section as exhaust air (an activated carbon recovery treatment of organics allows the controlled discharge to atmosphere); minor emissions are from the vacuum pumps and the plant can be provided with a vent recovery network, for continuous and non-continuous vents, connected to a combustor in order to lower all the plant emissions to a negligible amount.

Industrial applications

The Versalis Mantova plant is currently operating at a 300 kt/y capacity. Porto Torres plant has been revamped from 100 to 180 kt/y in 2000. In 1995 a phenol plant in East Germany was revamped from 60 to 160 kt/y. In 2015 a further 300 kt/y phenol capacity plant has come on stream in China, currently under revamping to 400 kt/y.

Product quality

Phenol

| | |
|---|----------------|
| Phenol (dry) | 99.99% wt min |
| Total organic impurities ^(*) | <10 ppm wt max |
| Color, APHA | 5 max |
| Freezing point | 40.85 °C min |
| Carbonyls, as Mesityl Oxide | <10 ppm wt max |

^(*) Excluding cresols
Application: Polycarbonate - Bisphenol-A

Acetone

| | |
|--------------------|---------------------------|
| Acetone (dry) | 99.95% wt min |
| Permanganate test | 4 hours min |
| Distillation range | 0.5 °C, including 56.1 °C |

AMS

| | |
|------------|--------------|
| AMS purity | 99.5% wt min |
|------------|--------------|

Application: Co-monomer for ABS, styrene and polycarbonate plastics

Main process parameters⁽¹⁾

| Material Balance | MT per MT Phenol |
|--------------------------------------|------------------|
| Raw material (Cumene) ⁽¹⁾ | 1.31 |
| By products (Acetone) | 0.618 |

⁽¹⁾ Assumes AMS is hydrogenated and recycled.

Process description

Phenol and acetone are produced from cumene in two steps: liquid phase oxidation of cumene to cumene hydroperoxide (CHP), followed by acid-catalyzed decomposition (cleavage) of CHP to phenol and acetone. Phenol, acetone, unconverted cumene, and by-products are then distilled in a series of distillation towers to recover high purity phenol and acetone products and to recover cumene to be recycled to reaction.

Fresh and recycle cumene are fed to a series of oxidizers where the cumene contacts air and is converted to CHP.

The oxidate is concentrated in a multi-stage cumene stripping system. Concentrated CHP flows directly to the cleavage unit where it is decomposed under precisely controlled conditions that are optimized to permit CHP decomposition without producing heavy by-products.

Cleavage effluent is neutralized before being sent to the first column of the acetone/phenol fractionation section to separate acetone, cumene, and light by-products from phenol and heavier. The distillate goes to a second column to produce acetone.

The bottoms of this column - a mixture of mainly cumene and by-product alpha-methylstyrene (AMS)

formed during cleavage - is sent to the AMS recovery system where the AMS is hydrogenated to cumene and the resultant cumene stream is recycled back to oxidation. The bottoms from the first fractionation column - containing phenol, some cumene and AMS and all the heavy by-products - is fractionated under vacuum to produce a crude phenol distillate, which further undergoes extractive distillation and stripping to make product phenol.

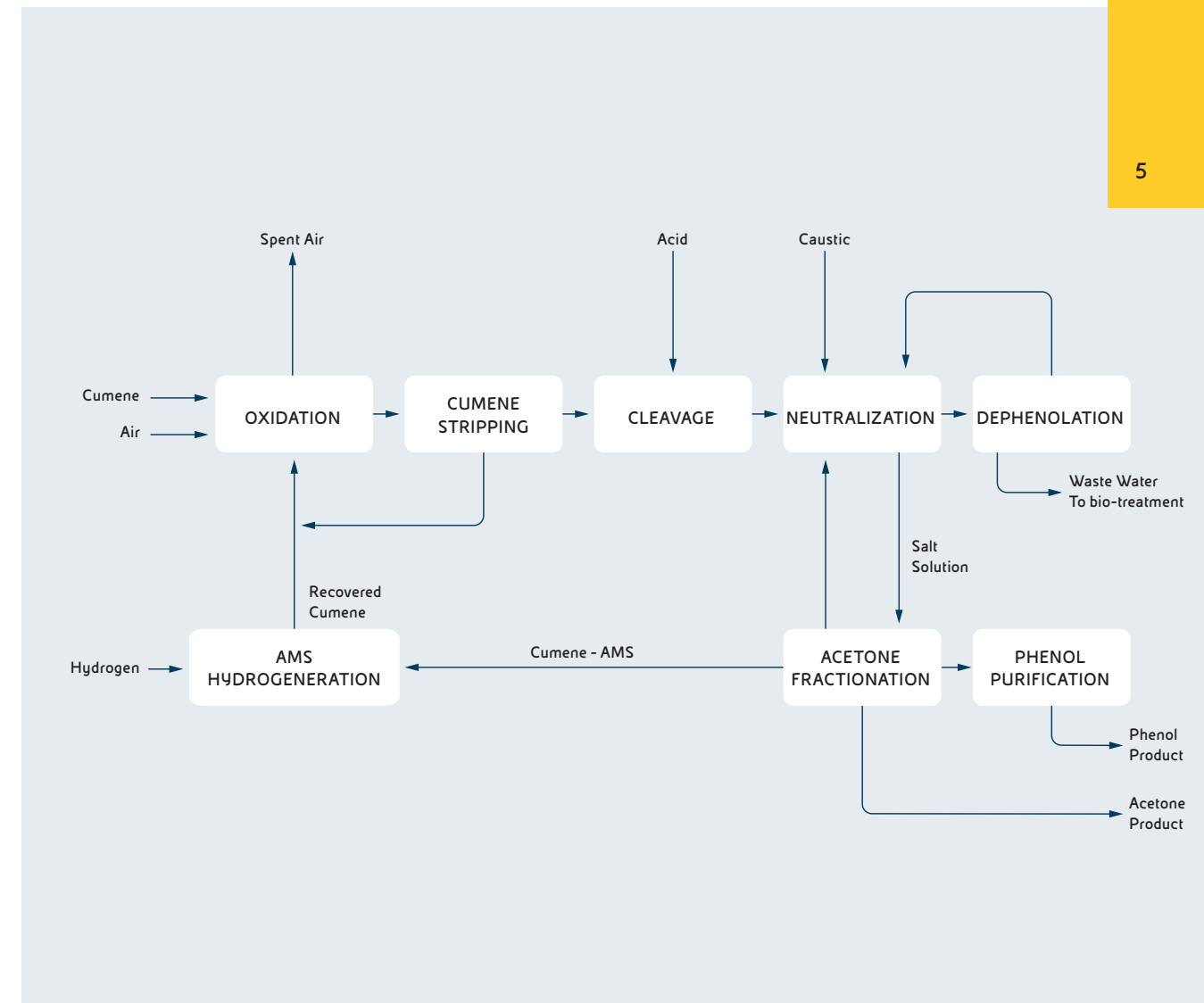
The phenol distillation bottoms contains all of the heavy by-products, acetophenone and some phenol and may be used as fuel.

All acetone - and phenol - containing vents are collected and chilled. Recovered phenol and acetone are recycled into the process, thus minimizing losses while at the same time reducing air emissions. After treatment, the vent gas can be discharged directly to atmosphere. All aqueous wastes and drains are collected in closed systems and then treated via extraction to remove phenol, which is recycled to the process. The resulting wastewater is of sufficiently high quality to be sent directly to an off-site bio-oxidation unit for final treatment before discharge.



fig. 1

Phenol & Acetone • 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, 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

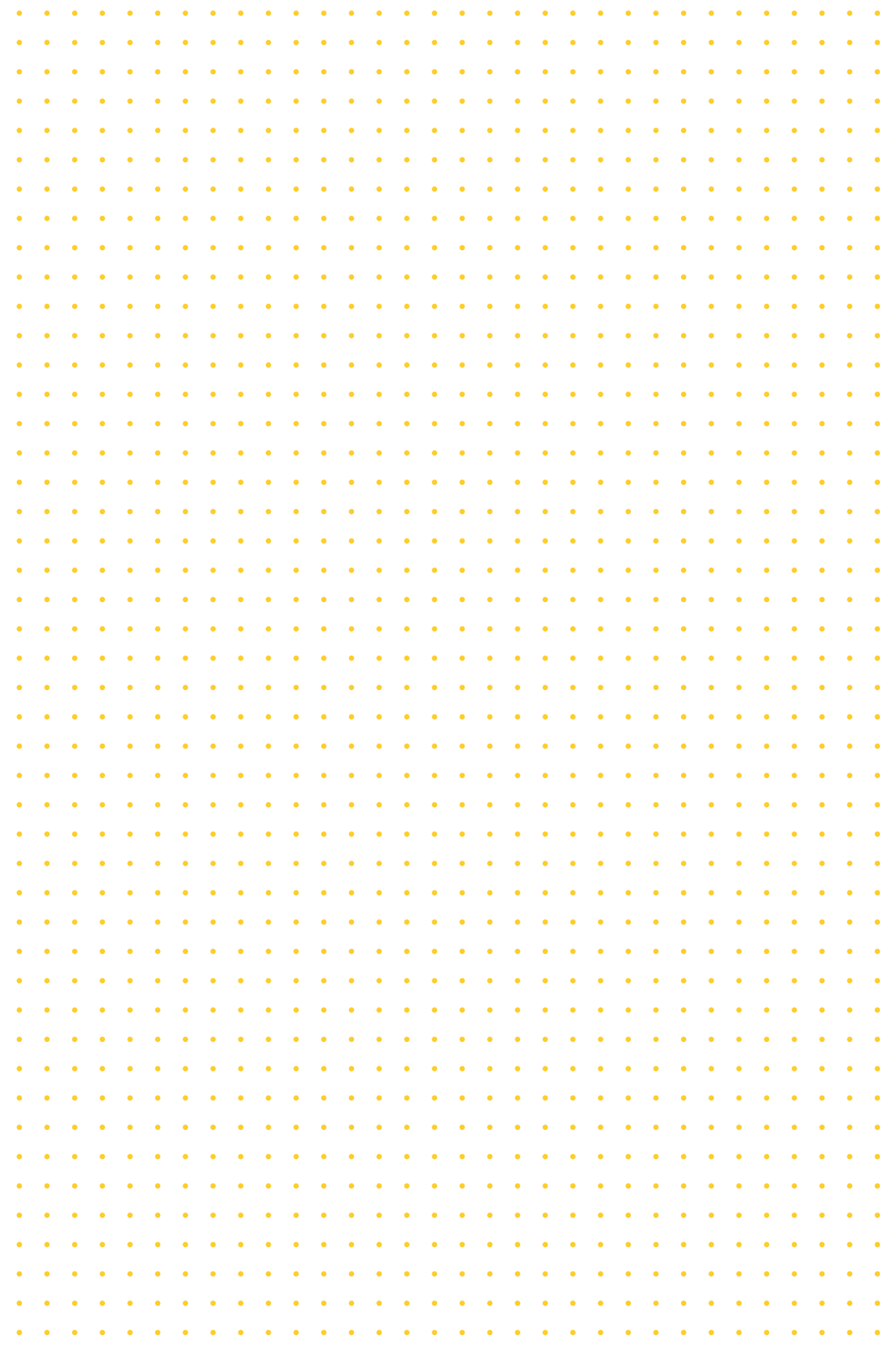
| |
|--|
| Ethylbenzene (with PBE-1 and PBE-2 zeolite based proprietary catalyst) |
| Styrene |
| GPPS |
| HIPS |
| EPS suspension polymerization |
| ABS continuous mass polymerization |
| SAN |

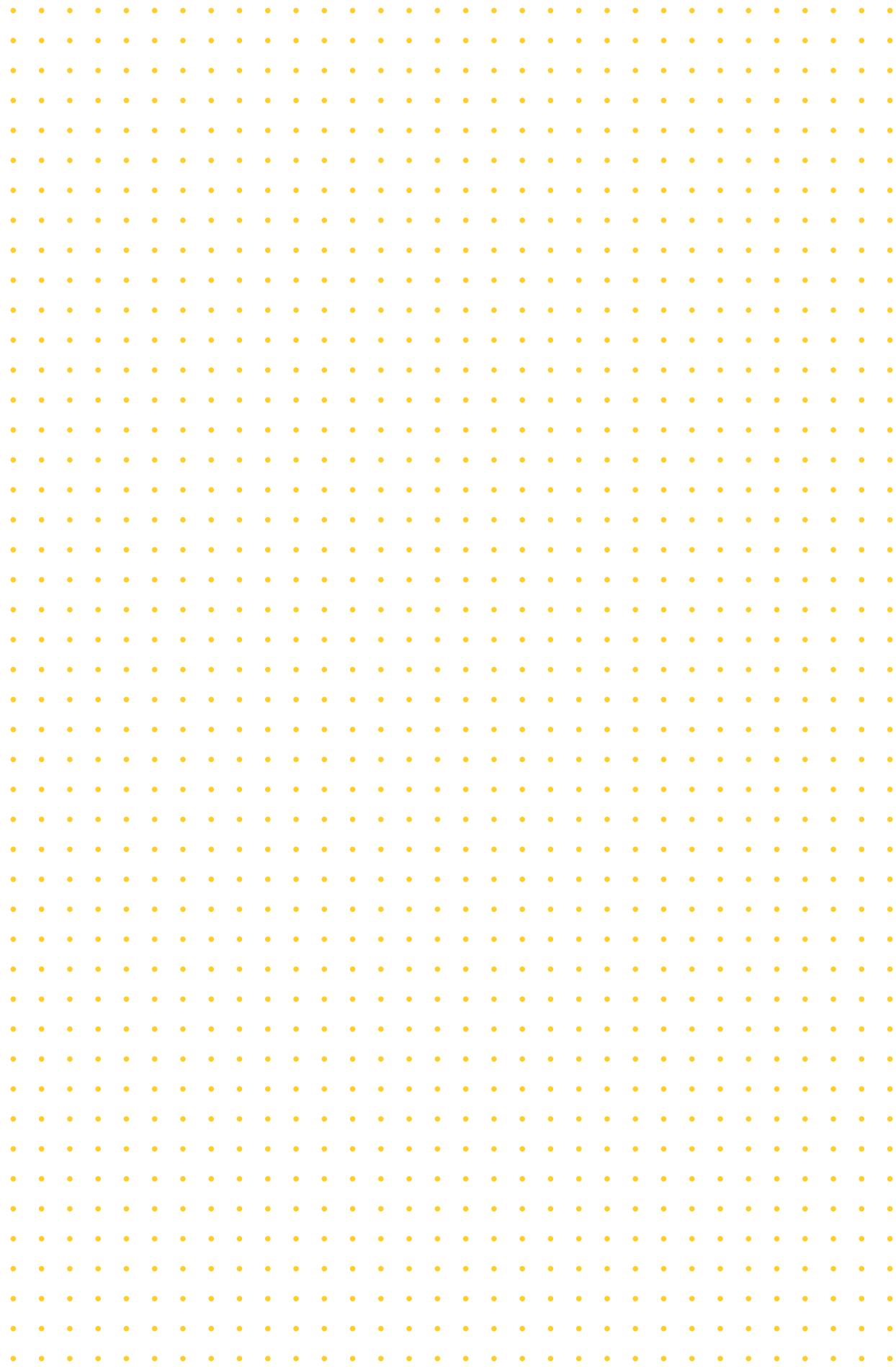
Polyethylene

| |
|------|
| LDPE |
| EVA |

Elastomers

| |
|----------------------|
| Emulsion-SBR |
| HSL Latexes |
| Solution-SBR |
| TPR |
| LCBR |
| HCBR |
| NBR |
| Carboxylated latexes |
| EP(D)M |







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