Absorbent Sponge Sheets from Pure Cellulose

For EDANA June 2010 by Calvin Woodings
CWC Ltd
Absorbent Sponge Sheets from Pure Cellulose

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Introduction

- Recently renewed interest in sponges in disposable hygienic products
  - P&G’s “Always Infinity” Femcare
  - Sponge tampons
  - Sponge cloths for wiping

- In 2008 CWC Ltd reviewed the feasibility of large scale regenerated cellulose sponge production for a major consumer products company.

- This presentation is an abstract of that review. *(N.B. The numbers have not been updated)*

- Its aim is to raise industry awareness of the potential for producing biodegradable absorbent sheets directly from natural cellulose.
Regenerated Cellulosics

- Regenerated cellulosics are products made by extracting natural cellulose from plant matter, dissolving it, shaping the solution into a fibre, film or sponge, and then regenerating the cellulose.

- The processes in use today are:
  - the viscose process where the cellulose is in solution as xanthate,
  - the lyocell process where cellulose dissolves directly in n-methyl morpholine n-oxide (NMMO).
  - the cuprammonium process where the cellulose is in solution in ammoniacal copper sulphate
  - Cellulose can also be acetylated to allow dissolution in acetone and formed into fibres, films, sponges etc.

- The viscose process is the most widespread and most versatile and is the only one used to make cellulosic sponges commercially.
Viscose Process

- Since the development of synthetic polymers and fibre based on cheap oil, the viscose share of the market declined but is now showing signs of recovery as the demand for biodegradable bio-based materials increases.
- It produces mainly staple fibres for spinning into yarns and for nonwoven production, and to produce continuous filament yarns for weaving.
- Yarns are use in apparel fabrics, home furnishing and industrial markets. Flame retardant versions are used in home furnishings, and high wet modulus versions in fashion apparel.
- For nonwovens high purity versions are produced: the main staple fibre applications being in disposable wipes, tampons and medical.
Cellulose dissolution processes: Viscose

Chemical recovery and recycling plant is a major component of viscose fibre production

N.B. Sponge processes do not require the use of zinc sulphate

Source: Courtaulds
The lyocell process was developed in the 1980’s as a minimal environmental impact process to produce cellulose fibre.

Lyocell staple technology (“Tencel” from Courtaulds) was commercialised in 1991 at prices 2-3 times those of viscose for the production of high quality fibres for high fashion garments.

The high fashion selling prices obtained proved unsustainable and the fibre is now sold into nonwovens, home furnishings and apparel at prices similar to viscose staple.

A massive expansion in regenerated cellulosics (~1million tonnes between 2005 and 2012) is underway but using viscose technology rather than lyocell.

Why?
Cellulose dissolution processes: Lyocell

Here the solvent used is n-methyl morpholine n-oxide resulting a simple physical rather than chemical dissolution process.

Viscose

- The fibre process is long and complex with many interacting variables determining final product type and quality.
- Requires strong caustic soda and carbon disulphide to form the sodium cellulose xanthate derivative which dissolves in dilute caustic.
- The viscose solution is low in viscosity and runs in low-pressure equipment.
- The main safety hazards are the flammability and toxicity of the $\text{CS}_2$ used, the toxicity of the $\text{H}_2\text{S}$ by-product and the corrosive nature of the soda used in dissolution, and the sulphuric acid used in regeneration.
- Chemical recovery and pollution abatement add to the capital costs.
Lyocell

- The process is simple and short.
- Pulp is dissolved directly in NMMO at high temperature and pressure.
- The resulting dope is very high in viscosity and needs expensive high pressure equipment through to spinning.
- Exothermic degradation of the solvent and oxidation of the cellulose is the main hazard.
- The NMMO is expensive and needs purifying and recovering with high efficiency.
- The capital costs are high.
- Current lyocell plants may be no more energy efficient than the latest viscose plants.
- Operating costs are at best comparable to those of a modern viscose plant.
Viscose fibres are regenerated by spinning the viscose dope into an acidic bath containing zinc sulphate and sodium sulphate. They are then stretched in air or in hot dilute spinbath which completes the orientation of the cellulose molecules and drives off the carbon disulphide and hydrogen sulphide formed as the xanthate is regenerated.

Fibre crimp is achieved chemically (skin core rupture creates bicomponency)

Washing is carried out on rollers for filament yarn or tow, or after the tow is cut into staple, on an open-mesh woven conveyor belt.

Washing stages include more hot dilute acid, hot dilute caustic to remove sulphur compounds, bleach, clean water and surfactants as needed for lubrication etc. in downstream processing.

Drying is on drums, or conveyor belts. Packages are bobbins or cheeses for the continuous filament yarns, and highly compressed bales for staple fibre or tow.
The dope is extruded vertically downwards through an air-gap with cross-draught into a dilute solution of the solvent.

Draw-down orients the cellulose in the filaments and crystallisation occurs as the solvent is washed out.

High wet modulus fibres with a tendency to fibrillate into microfibres result naturally.

If the tow is cut before washing fibre some crimp can be obtained by squeezing the still-plastic filaments on the wash conveyor.

Washing is with counter-current water.

Drying is by hot-air on drums.

In the Courtaulds process, the dry tow was crimped mechanically prior to cutting and baling.
Viscose Sponges: The Spontex Industrial Range

- Cellulose Sticks
- Compressed Pieces
- Cellulose Blocks
- Compressed Sheets
- Sponge Cloth Rolls
- Tiger Rag
- Printed Pieces

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Introduction to Sponge Technology:

- Cellulose sponges and the technology to make them developed when the viscose fibre process was expanding rapidly and before strict environmental controls dramatically increased the costs of their production.
- Early sponge producers could buy viscose dope from large scale viscose operations and avoid the need for CS$_2$ and caustic soda handling.
- The complexities and costs of the viscose process now make cellulosic sponges a premium priced product compared with synthetic sponge.
- It remains a good substitute for the more expensive natural sponge, is widely used in household products, and has high value niche applications in medical products.
Introduction to Sponge Technology:

- Cellulose sponge manufacture using the viscose process is however in long-term decline.
- Plants in Japan, India, Scandinavia, UK, and 2 of the 3 plants in China have all closed.
- 3M “bucked the trend” of the last 20 years, by buying out O-Cel-O and Nylonge in the USA, but have spent $millions getting these plants working within EPA regulations.
- This was part of 3M’s strategy of increasing the proportion of group sales direct to retailers.
- Spontex remain the largest producer with plants in France Spain and the USA(?) but now operate with a much reduced product range and minimal R&D.
- A plant built in Mexico 2005, which made excellent quality sponge, closed after 1 year of operation and then restarted.
- Cellulose sponge production by the lyocell process has been developed but appears not to have progressed beyond the laboratory scale.
Viscose Sponge Technology: Chemical Pathways

Source: AMPA Associates
Viscose Sponge Technology

- Viscose sponge can be made as sheets or buns or blocks which are then cut to the desired shape or extruded continuously into rods or sheets with a variety of cross sections.
- Pore shape is defined by the shape of the Glaubers salt added to the viscose in the mixer.
- In the sheet and rod processes, the dope is extruded through a die onto a conveyor for regeneration and then washed on conveyors or over rollers immersed in wash liquors.
- In the bun or block process the dope is poured into a rectangular mould and regenerated by heat and/or acid prior to washing and bleaching.
- A block is usually 1m x 1m x 0.5m
- A bun is usually 1m x 0.15m x 0.1m, although larger “superbuns” are now made
- “Multiblock” (2m x 2m x 1m) is now available and this is usually cut to “block” size for conversion.
Sponge v. Fibre: A fundamental difference

- Fibres, being made by extrusion through holes of 50-100 micron diameter, require a near perfect cellulose solution, free from undissolved pulp fibres, air bubbles and gels.

- Sponges are made in blocks or by extrusion through slots as wide as the sponge is thick. Crystals, air and fibres are added deliberately.

- Cost of equipment, pulp, chemicals and filtration/deaeration are therefore potentially much lower for a sponge process than for a fibre process – especially on the viscose route.

- Why is sponge expensive compared with fibre?
- Viscose fibre plants continuously produce >100,000 tonnes of a few fibre types.
- Sponge plants produce <5000 tonnes of many types, often using batch processes.
Viscose Sponge v. Fibre Technology: Pulp

- Pulp contains three main types of cellulose: alpha, beta and gamma.
- Beta and gamma are short-chained and form hemi cellulose which is readily lost from the viscose process and will weaken the final structure.
- Higher alpha pulps are more expensive than lower alpha, but lower alpha pulps give a lower sponge yield.
- Dissolving Pulp (high alpha) as used for fibre-making is also used in sponge production. This comes from farmed hardwood or softwood plantations.
- High alpha pulp from cotton is commonly used for viscose in China and for cuprammonium rayon production.
- “Low-tech” sponge processes use the same expensive cellulose sources as the “high tech” fibre processes.
Viscose Sponge v. Fibre Technology: Xanthate Making

- In the viscose fibre process, steeping with caustic, shredding, reaction with carbon disulphide (xanthation), dissolution of the xanthate, filtration and deaeration and ageing of the resulting viscose is a large and complex chemical engineering operation with miles of pipework and a proliferation of pumps and filters.

- In the sponge process all of the above can take place in a single suitably designed enclosed mixing vessel, dissolving soda being added to the xanthate to form the viscose prior to adding the pore former.

- In the sponge process reinforcing fibres (woodpulp, cotton, viscose, recycled fibres at lengths from 3 – 15mm) can be premixed with the dissolving soda if required.
Viscose Sponge Technology: Sponge forming.

- The paste of viscose, crystals, fibres and pigments is pumped using a screw conveyor or extruder into a mould (for blocks) or through a slot-dye for sponge-cloth.
- Sponge-cloth can be reinforced with scrims, spunbond or yarns sandwiched between the output of two dies.
- The block-sponge moulds have electrodes in opposing walls to allow the mass to be heated to above the melting point of the crystals. This heat simultaneously regenerates the cellulose and, by dissolving the crystals, forms the pores.
- For sponge cloth, the paste is cast onto a heated stainless steel conveyor which regenerates and forms the pores, or onto a porous conveyor which can be immersed in hot water or dilute acid.
- CS$_2$ and H$_2$S are emitted during regeneration.
Sponge-blocks can be washed whole or after cutting into smaller pieces, in a series of baths. Sponge cloth can be washed continuously on a conveyor or over rollers immersed in the wash liquors.

Typical wash sequences will include dilute alkali to solublise sulphurous bi-products, an alkaline water wash to remove the bi-products, bleach and a series of counter-current water washes.

Plasticiser e.g. MgCl$_2$ at about 5% on cellulose, or surfactants can be added at a finishing stage before drying.

Sponges can be sold wet (~50% moisture) or can be sliced into sheet before compression and RF or through-air drying.
Mapa Spontex, recently acquired by Jarden from Hutchinson, part of the Total group, is the largest cellulose sponge producer.

They have 2 plants in France, Facel with a capacity of ~1100 tonnes/year and Beauvais with a capacity of ~3500 tonnes/year.

Their Spanish plant (Barcelona) has a capacity of ~3500 tpa.

Their US Plant (Columbia-TN) has a capacity of ~3000 tonnes.

They have recently reduced the range of products produced, and cut back the R&D operation.

They do make compressed sponges and also extrude rods.
Leading producers of Sponges: 3M

**Tonawanda plant**
- 3M purchased this 1947 O-Cel-O™ sponge plant in 1990 and has invested heavily to continue to expand the operation and improve the manufacturing processes.
- In 2001, 3M’s other sponge making facility in Prairie du Chein, Wisconsin, was closed and equipment moved to the Tonawanda plant.
- 3M continues to make investments in equipment, research, new technologies, and marketing to ensure Tonawanda remains the world's largest cellulose sponge producing facility. (capacity estimate – 4,000 tpa)

**Elyria Plant**
- The acquisition of Nylonge Corp in October 2006 expanded 3M’s global sponge manufacturing capabilities.
- Nylonge’s line of products includes cellulose sponges, scrub sponges, sponge block, sponge cloth, dust cloths and vinyl gloves.
- Elyria sponge capacity is estimated at 3,250 tonnes.
- 3M attempted to buy Spontex but was prevented by the French Government.
Freudenberg acquired the Wettex (Sweden) and Enka (Germany) sponge operations in 1990.

The Enka operation was sold on to Hoechst/Kalle while the Wettex operation continues to produce sponge cloth for the Freudenberg Household Products division.

Hoechst divested the Kalle sponge operation to private equity in 1997.

The Wettex (Sweden) capacity is estimated at 2000 tpa.

Wettex sponge is also marketed by Johnson Wax in Australia.
Kalle, one of the world’s leading producers of viscose-based sausage casings, produces sponge cloth used in households and for various industrial and medical applications.

The company has invested in developing and implementing an integrated environmental recycling and disposal facility which has contributed to it becoming a reference company throughout the industry.

CVC Capital Partners acquired Kalle in 1997, the company was a subsidiary of Hoechst AG


Montagu Private Equity sold Kalle to Silverfleet Capital in Sept 2009

Sponge capacity was estimated at ~2000 tonnes.
Leading Producers of Sponge: Zibo Lot, China

- Claim to make any shape, size or colour cellulose sponge, with or without skin, in sheet or block form, compressed or not.
- Claim to operate 6 sponge production lines.
- They appear to make only buns (which they describe as blocks) and cut sheet from bun.
- They have shipped wet sponge to EU converters. (mould issues?)
- They probably use cotton linter pulp instead of woodpulp for viscose making
STC began in 2005 when a group of entrepreneurs and engineers from Nylonge and Wipex US (Sponge importers) came together to build a state of the art sponge cellulose manufacturing plant.

The factory was completed in the summer of 2006 in Tetla, Tlaxcalca, Mexico. 2008 capacity = approx. 30,000 cellulose sponge blocks per year.

They claim proprietary technology to make salt and reuse it, giving a significant cost saving and quality benefit; regulation of the salt’s size, being critical in determining the sponge’s look and feel.

They claim to be one of the cleanest, environmentally sound cellulose factories on the planet, reusing 99.97% of waste.

The central location in Mexico gives lower distribution costs for customers and provides quick turnarounds. Being in Mexico it also avoids costly tariffs importing goods into the US versus importing from China.

They supply the US market.
## Leading Producers of Viscose Sponge

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- *Estimate based on their estimated consumption of DP in 2007
- **Estimate based on market intelligence regarding their capacity. (Finished sponge is DP+fibre+additives)
For household sponge cloth which use fibrous additions for reinforcement, the complete dissolution of cellulose is clearly unnecessary.

Kamide et al working in Asahi's Fundamental (Fibre) Research Laboratory described fibres spun from soda solutions of cellulose. Steam-explosion was used to improve the accessibility of the cellulose chains prior to contact with the sodium hydroxide.

Struszczyk et al used cellulase enzymes to modify the structure of cellulose to allow it to dissolve in soda.

Courtaulds Research obtained partial pulp dissolution in 9% caustic at temperatures below -10°C in the 1970’s. These fibrous dopes could be cast into films and may be worth reinvestigating as a low-cost low-environmental impact route to form pulp-fibre reinforced sponges.

While these soda-only cellulose dissolution routes make poor solutions and fibres with properties inferior to viscose rayon, they may prove more than adequate for sponge production.
Possible Future Developments: Pore forming without Salt

- Sub-zero viscose processing has the potential for using ice crystals as a pore former.
- The ice-crystals could be formed in the same cooled pulper which is used to “dissolve” the woodpulp.
- Reinforcing fibres could be added here if the undissolved pulp fibre provides insufficient reinforcement.
- The sponge precursor paste could be extruded onto a hot conveyor, melting the ice and providing a support for water washing.
- Extracted soda could be cleaned, concentrated and reused.
Possible Future Developments: Absorbent Nonwovens?

- Sub-zero xanthate-free fibre-reinforced sponge precursor formed in a pulper could be extruded wide, thin and fast onto a forming wire not unlike those used for spunbond production...
- ...in fact rather like those used for producing sheets of cardboard or wood-pulp...
- ...which is usually made in a large mill which has large pulpers and is used to handling the sort of materials required for these sponges.
- These mills already make large rolls of wide absorbent.
Possible Future Developments: Absorbent Nonwovens?

If it’s not already clear:

- We believe the technology exists to produce 100% biodegradable fibre reinforced sponge nonwovens on a very large scale direct from woodpulp, maybe on-site at a pulp mill.
- All we need is a market requiring ~50,000 tonnes of biodegradable absorbent sheet which would be rather like a strong and bulky air-laid nonwoven.
- We believe the costs of this fibrous sponge sheet would be more similar to pulp costs than current nonwoven wipe costs.
Absorbent Sponge Sheets from Pure Cellulose

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