

## INVESTMENT IN FIBERS AS A CHALLENGE FOR R&D

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The recent announcements of Lenzing AG to expand its Austrian viscose fiber plant in Lenzing and its Lyocell fiber plant in Heiligenkreuz; Austria, came somewhat as a surprise to the textile world. It seems that the community believes that the current state of the industry could only produce news of plant closures. Some of the players obviously fail to understand a decision to increase fiber capacities in Western Europe. For Lenzing it will be an increase of more than 100.000 tons/year in less than a decade, which is more than just compensating for the cumulative reductions of other producers within the same period. The question remains whether Lenzing is an exception or whether it would have been better to follow the trend.

There have been a considerable number of plant closures in recent years. Many of the big, traditional fiber producers have completely given up their activities in the fiber field. Their market analysis has taught them about the long-term shrinking consumption of their established products and the increased pressure on the margins. The consequence in most cases was a “milking strategy”, sooner or later ending in mill closures during one of the next downs in the business cycle, often with the expectation of a better utilization of the remaining capacities. However the pessimistic message of this type of withdrawals often resulted in the complete disappearance of the corresponding markets. Also Lenzing had to suffer from this type of decisions when their renowned joint venture partner insisted in closing their joint polyester staple fiber plant in Austria.

But is it really true that Europe is inevitably caught in the same trend as the US, where the textile industry and the fiber producers servicing it almost disappeared in the last decade? Surprisingly not only are capacities in man-made cellulose increasing again in Western Europe, reaching levels even above those of the late

1980s when the textile world was said to be still doing well (figure 1). It is also commodities, such as polyester staple, where in spite of several plant closures by traditional producers even small entrepreneurs identified business opportunities and started investing in new grassroots capacities. The face value of the market assessment of many of the key players clearly does not reflect the whole picture!

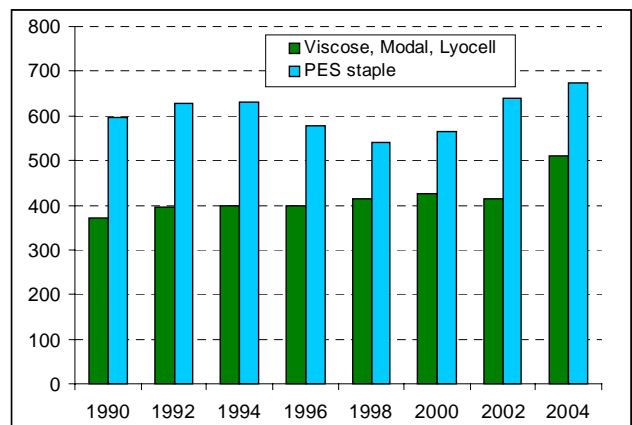


Figure 1. Production capacities in Western Europe (tpa).

Everybody knows that there has been a huge change in the structure of the markets and there are good reasons for the depressed moods of many players in the industry. It is true that the migration of textile manufacturing to cheap-labor countries has completely changed the scenarios. The textile industry has been shaken and is still being shaken by the pressure of cheap imports.

The market is neither willing nor able to continue paying the profit margins for standard products expected by the fiber producers. But is reduction of capacities the only possible consequence of such a process? The future of the industry rather seems to deal with the old issues of taking up a challenge and working on converting it into a chance by starting with the “home exercise” to reduce the cost basis, to solve environmental problems, to adjust the quality to the increasingly demanding downstream processing technologies,

to find new market segments, and to support the customers in doing this by offering new innovative fibers! But of course this is not suitable for a “milking strategy”! Lenzing’s capital investments, exceeding the 100 million Euro level, can only be understood in view of many years of this type of “home exercise” - and a lot of it has to do with constant investment in R&D. Lenzing has been able to solve the environmental challenges inherent to the technologies employed and now is a model for environmentally friendly viscose fiber production. Innovative processes have been developed to produce fine chemicals from former pulping process emissions, which now considerably reduce the costs for dissolving pulp, the major raw material.

Continuous development efforts have resulted in a significant improvement of Lenzing’s product portfolio. The wide technological basis available to Lenzing - with the viscose, modal, and recently the Lyocell process - offers wide possibilities for producing all the variety of fibers for the special needs of the market. It is because of a drastic improvement of the technological properties that they are able to meet the demanding needs of today’s high performance textile industries in Western Europe. Support of innovative looks, new drapes, new hands and special effects are equally crucial for success in the fast-changing and fashion-driven textile world.

From about 30% only 10 years ago, Lenzing is now selling more than 60% of its production into

specialty market segments. Micro-fibers, spun-dyed fibers, UV-protection and flame retardant properties are but a few of the features in that field. New fibers with further enhanced moisture absorbency and water retention are servicing additional nonwovens and technical applications, which are presently the fastest growing market segments in Western Europe. A new fiber with improved dyeing properties offers substantial advantages to the downstream processing industries and to fashion designers.

In contrast to the widespread opinion, there are several examples that companies producing or processing fibers in Western Europe still have a chance to prosper, if they take the challenge and refocus on the traditional strengths of European manufacturing industries. The recent incidents in some of the service- and “new markets”-industries in the US have shown that benchmarks of continuous upward trends are not realistic, despite occasional impressions that this is so.

We have good chances if we concentrate on flexibility, efficiency and diversification, on innovative products and new technologies. One of the strongest assets in this context is the excellent education of the available work force. But this also requires a culture of stability and long-term thinking. Similar to production plants, which cannot not work without proper maintenance and capital expenditures, innovative products and new technologies will not be available without consistent R&D as well as an efficient and flexible high-quality work force, which also requires proper care and handling.

# VISCOSE STAPLE FIBER - HISTORY AND TRADE FLOW OF FIBER AND DOWNSTREAM TEXTILE PRODUCTS

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## Production and consumption of viscose staple fiber

Viscose staple fiber still plays a significant role in the world fiber market, although if we look back 30 years, it lost market share to the fast growing synthetic fibers and cotton. Total world fiber consumption increased from 22 million tons in 1970 to over 50 million tons in 2001. This includes both natural and man-made fibers, staple and filaments (Figure 1).

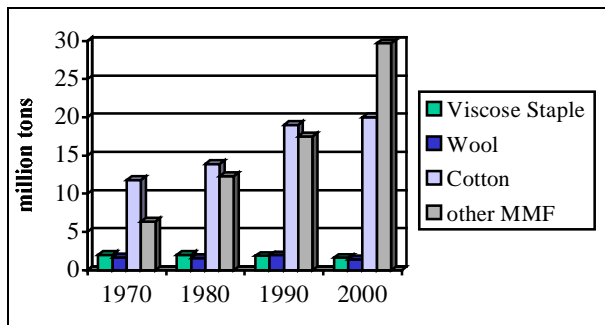


Figure 1. World consumption of fibers.

Viscose staple consumption was 2 million tons worldwide in 1970 and was only 1.6 million in 2001, mainly due to a sharp decline in Eastern Europe after the political changes in the late 1980s. In fact, viscose staple consumption has grown slightly, if we disregard the development in Eastern Europe (Figures 2 and 3).

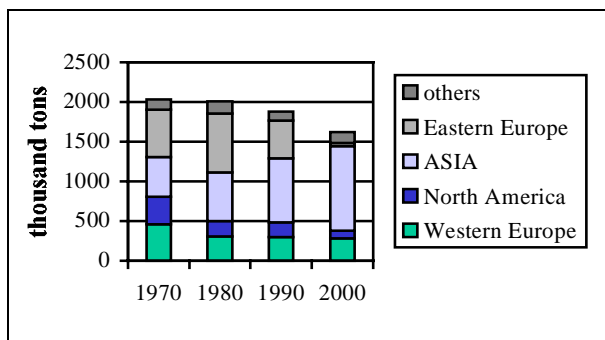


Figure 2. World consumption of viscose staple went down mainly due to development in Eastern Europe.

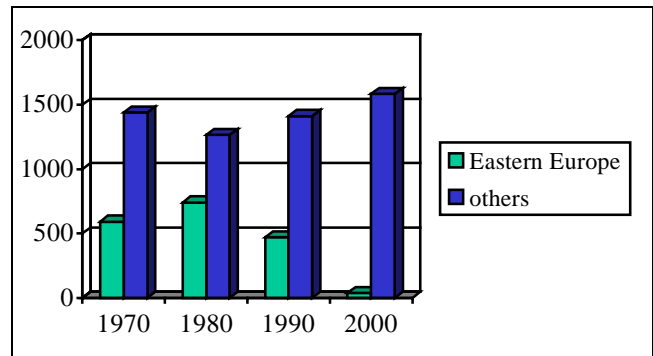


Figure 3. Viscose consumption increased.

As with other fibers, viscose staple fiber mill consumption moved significantly to Asia from other parts of the world (Figures 4 and 5). Today, the Asian countries account for three quarters of the world mill consumption of viscose staple for textile applications, while Western Europe is dominant in mill consumption for nonwovens applications (Figure 6).

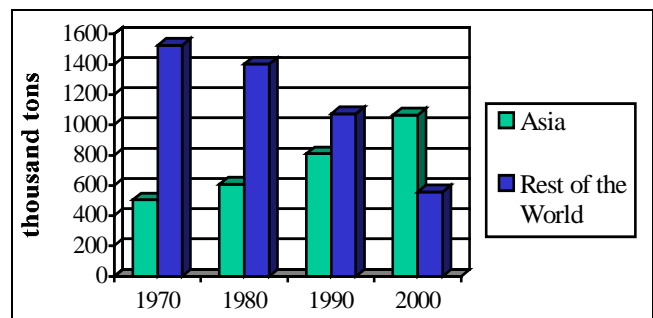


Figure 4. Shift of viscose staple fiber consumption to Asia.

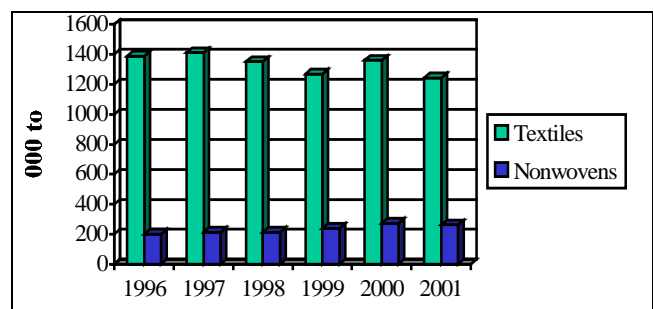
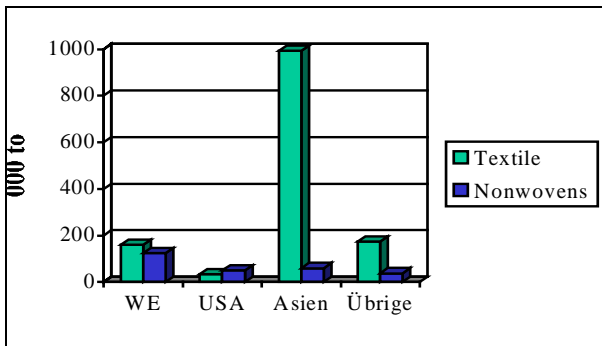
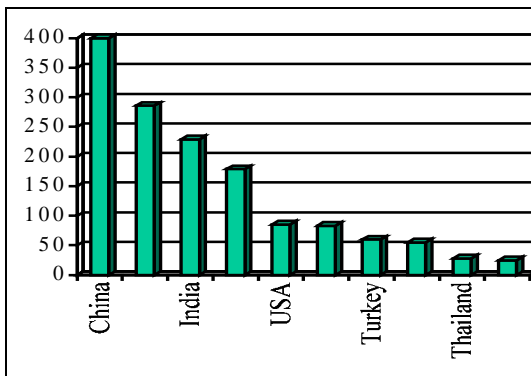


Figure 5. Nonwovens share of world consumption of viscose staple is rising.



**Figure 6.** Asia processes 75 % of viscose staple for textiles, Western Europe is dominant in nonwovens.

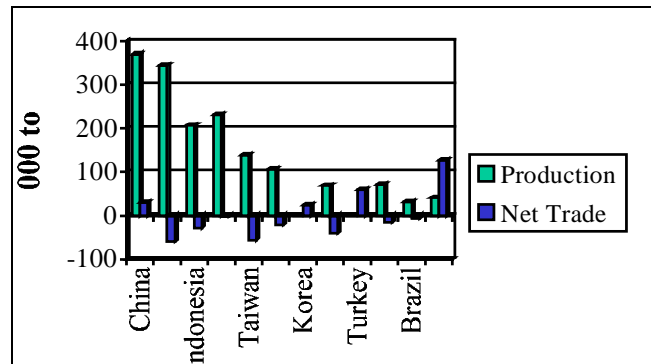
China, Western Europe, India and Indonesia are the countries with the highest mill consumption of viscose staple fiber today, followed by the USA, Taiwan, Turkey, Japan, Thailand and Korea. These 10 countries accounted for 90 % of the total world consumption in 2000, as shown in Figure 7.



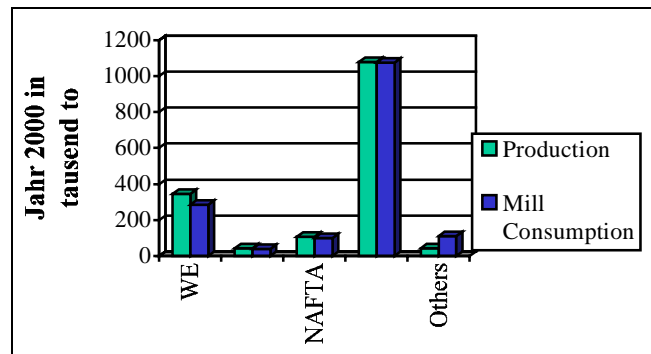
**Figure 7.** Viscose mill consumption – the top 10 countries account for 90 % of the world consumption in 2000.

### Fiber Trade Flow

With textile activities moving towards the Far East in the past 20 to 30 years, fiber capacities have also been established in Asia. Compared to the “old days” when Europe, Japan and the USA used to export huge quantities of viscose staple, today the net fiber trade volumes are relatively small, as shown in Figure 8 for the top 10 countries. The most important net-exporters are Western Europe, Taiwan, Thailand and Indonesia; the major net-importers are Turkey, China and South Korea. There are substantial volumes of fibers moving around the world, but in terms of net trade the situation is relatively balanced. This is particularly true if we look at trade blocks rather than individual countries (Figure 9).



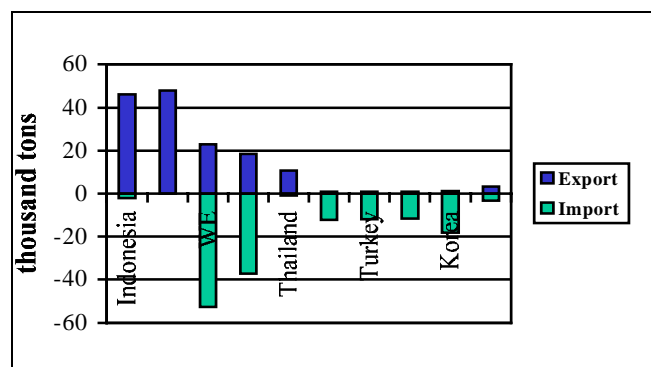
**Figure 8.** Viscose fiber trade flow 2000.



**Figure 9.** Within the trade blocs, production and consumption of viscose staple is rather balanced.

### Yarn Trade Flow

The effects of globalization can also be seen in the substantial trade of viscose spun yarns. India, Indonesia and Thailand are the most important net-exporters today. Western Europe and China also are important export countries, but with high imports actually net importers. Importing countries with hardly any viscose spun yarn exports are South Korea, USA, Turkey and Japan. Taiwan’s imports and exports are approximately balanced. In total, the imports and exports of the top 10 countries shown in Figure 10 add up to 150.000 tons each.

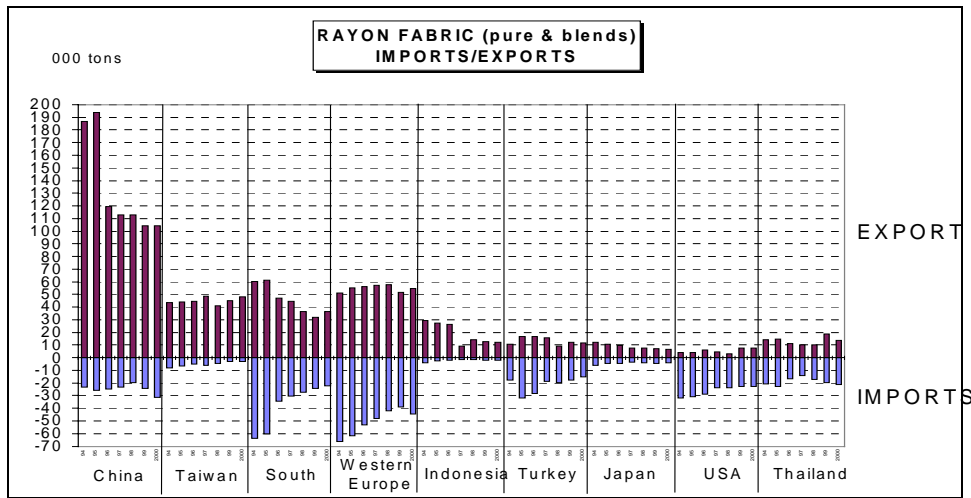


**Figure 10.** The total of yarn imports and exports is balanced with 150.000 tons each in the year 2000.

**Fabric Trade Flow**

As shown in Figure 11, there is significant trade in viscose fabrics, though declining over the

last few years. This effect may partly be the result of more fabrics being used in their own “making-up” industry in countries, such as China and Indonesia.

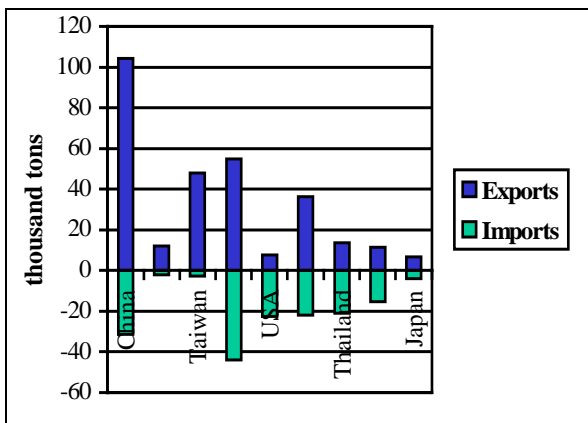


**Figure 11.** Rayon fabric imports and exports.

If we again look at the most important viscose markets in the year 2000, we see exports of 300 thousand tons of viscose fabrics – double the volume of yarn trade –, but imports of only 165 thousand tons (Figure 12). The balance is fabric export to typical garment manufacturing countries in Asia, Eastern Europe, North Africa, Near/Middle East and South/Central America.

**Final consumption of products made of viscose staple fiber**

There are no statistics available that would show the trade flow of garments made of viscose staple fiber. However, based on estimates we can conclude that Western Europe and the United States still are the most important consumer markets for final products made of viscose fiber. Together they account for approximately 40 % of total world consumption, compared to a 10 % share of world population. Western Europe sticks out with an estimated share of 26 % of world consumption of final viscose products, compared to 6 % share of world population. These numbers refer to final consumption of all viscose staple fiber products, both textile and nonwovens in the year 2000. Looking at the textile sector only, import penetration is increasing in these major consumer markets, particularly in the United States and mainly in the form of ready-made garments. Comparing final consumption of viscose textile products with mill consumption of viscose staple fiber for textile applications, the import penetration in 2000 was 46 % in Western Europe and already 76 % in the United States, and growing.



**Figure 12.** Total exports of viscose fabrics were 300.000 tons compared to 165.000 tons imports in the year 2000.

There is a distinctive difference in the trade pattern between grey fabrics and finished fabrics. China is by far the largest exporter of grey viscose fabrics, followed by Indonesia. The bulk of these grey fabrics go to Western Europe, South Korea, Thailand and Turkey, from where a substantial part is re-exported in form of finished, dyed or printed fabrics.

It will be interesting to watch the development after all quotas will be eliminated in 2005 as a result of the Uruguay round.

## IMPORTANT TRENDS AFFECTING THE ASIAN VISCOSE MARKET

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### Introduction

The recent development of regional trade blocks, such as NAFTA, is having a huge impact on Asian textile producers. As a result, viscose textile product producers will have to look at their present strategies to find new competitive advantages to sustain their business in the future.

### Development of trade blocks

With the implementation of NAFTA at the end of the 1990s, the textile imports into the USA have made a drastic shift to Mexico and the Caribbean Basin suppliers. Imports from China and other Asian producers have dropped dramatically. They have lost significant market share to Mexico. With the implementation of the Caribbean Basin Initiative (CBI) imports from these countries will increase greatly in the future. In a similar move, Europe is also shifting more textile imports away from Asia to Eastern European and North African countries.

The much-discussed WTO will have little effect on tariffs compared to regional agreements. Under the WTO agreement the US import duty on a pair of cotton pants, for example, will decline from 17.7 % today to 16.6 % in 2004. In contrast, under the NAFTA agreement the import duties on most textiles from Mexico and Canada are already at or near zero.

As a result of such measures, textile imports from Mexico have grown from 50 % of the level of imports from China in 1994 to now 200 % of the imports from China in 1999. Apparel imports from Mexico and the CBI nations have grown from 16 % in 1994 to 33 % of all imports in 1999. China, on the other hand, has dropped from 11 % in 1994 to 6.6 % in 1999.

The resulting shift in regional trade will have a staggering impact on Asian textile exports. The USA and Europe are by far the largest importers of textiles. Asian producers have always assumed that their cost advantages will allow them to continue their export growth to these

regions indefinitely. With the development of regional trade pacts, the situation has clearly changed and Asian producers must now brace themselves for reducing exports to these regions in the future (Figures 1 - 3).

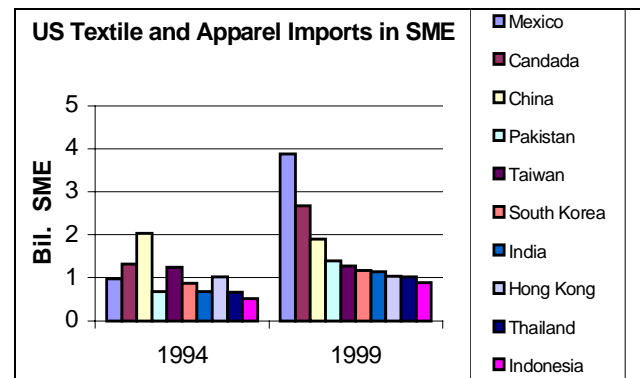


Figure 1. Mexico became the leading textile and apparel exporter to the USA after NAFTA.

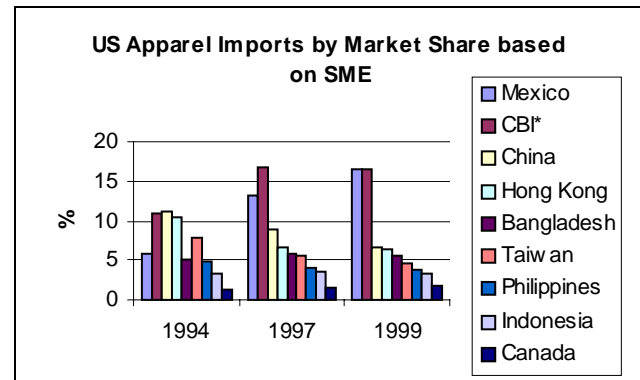


Figure 2. Mexico and CBI countries are replacing Asian apparel imports.

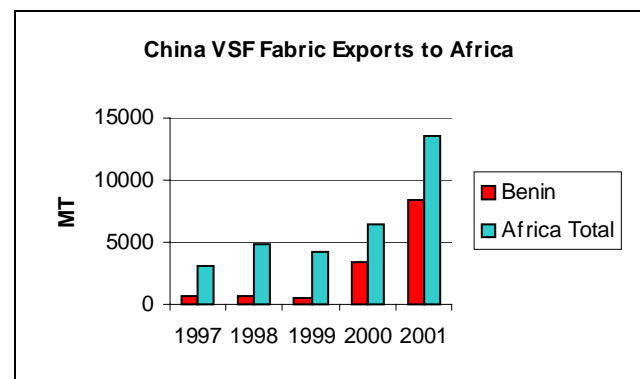


Figure 3. Sub-Sahara Africa becomes new player in VSF textile trade.

## Risks of export dependency

The focus on textile exports has left Asian textile producers vulnerable. Exporters are open to a number of risks compared to those selling in their domestic markets. The added costs of transportation, duties, transaction costs, storage costs and distance to the customer can be higher than advantages in labor or other costs.

A variable cost comparison between a European viscose yarn spinner and an Indonesian spinner shows that the Indonesian producer has a \$0.31/kg advantage (Figure 4). After adding capital costs, where developing nations, such as Indonesia, are at a disadvantage, the difference has reduced to \$0.20/kg. After adding transportation, duties and storage costs, the difference changes to \$0.13/kg to the advantage of the European spinner. Currency fluctuations can also greatly influence any cost advantage a producer might enjoy. Finally, since higher-value items tend to be short-lived, most imports are limited to easy to forecast commodity items, where margins are low to begin with.

Another risk of export dependence is the exposure to changes in foreign government policies. Duties, quotas, export subsidies and other trade policy instruments can change the playing field overnight. The inequalities created by these policies can be very significant and difficult to overcome with production cost advantages.

## Status of Indonesian viscose yarn and fabric exports

The Indonesian viscose industry is very dependent upon yarn and fabric exports. Applying the information gained about global textile trade trends, we will look at the risks and opportunities for the Indonesian viscose yarn and fabric producers (Figures 6-12).

Since 1990, viscose yarn exports from Indonesia have increased sharply. Up until 1995, viscose fabric exports exceeded yarn exports on a volume basis. In 1995, viscose fabric exports started to decline while yarn exports continued to grow. This change in trends was a result of expansions in spinning capacity with new equipment, enabling yarn producers to compete in European and other high-quality markets.

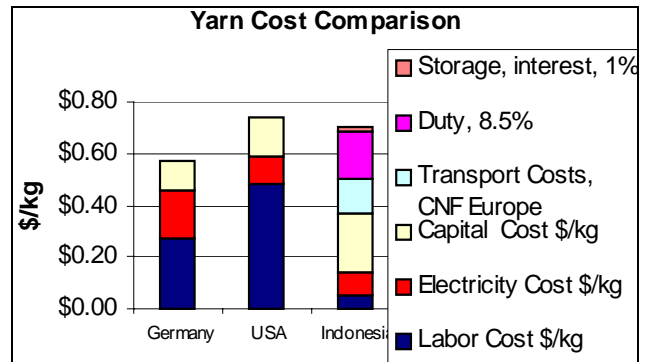


Figure 4. Yarn production cost comparison.

The viscose yarn imports by the major importing countries have been growing on average by 4% annually. On the other hand, Indonesian viscose yarn exports grew by 26% in 1999 and 10% in 2000 (Figure 5). This imbalance implies that the rapid growth in exports can only be maintained through aggressive growth in market share. This is becoming increasingly difficult as Indian yarn exports are growing rapidly due to the export subsidies given by the Indian government to yarn exporters. In addition, Indonesia has already become the major supplier to most of the major markets, putting Indonesian spinners on the defensive rather than offensive.

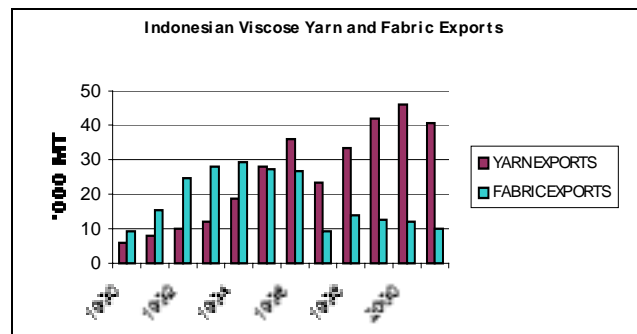


Figure 5. Indonesian VSF yarn exports have continued to grow, but fabric exports have declined dramatically.

After a sharp drop from 1995 to 1997, viscose fabric imports by the major importing countries have remained flat. Indonesian weavers have lost market share in most of the major markets. In the UK, for example, imports from Indonesia have declined from 6.400 MT in 1995 to 1.200 MT in 2000 while imports from Taiwan have grown from 2.300 MT in 1997 to 5.000 MT in 2000. Thailand is another major importer of viscose fabrics. China has constantly maintained a market share of over 85 % over the past 5 years while imports from Indonesia have declined from 4 % to 2 % in the same period.

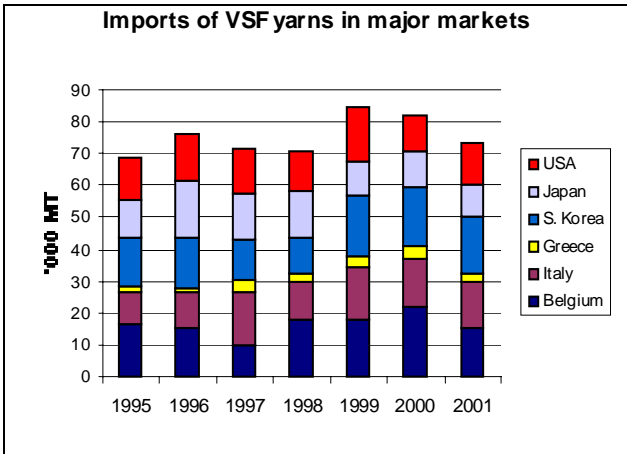


Figure 6. Minimal growth in major VSF yarn importing markets.

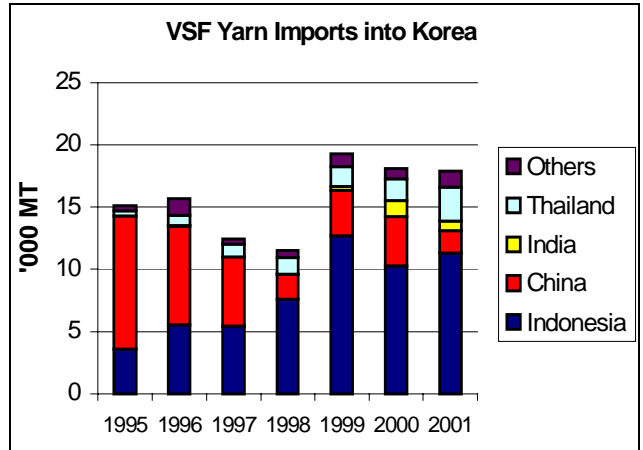


Figure 9. Indonesia has increased its market share of VSF yarns imported into Korea from 23 % in 1995 to 63 % in 2001.

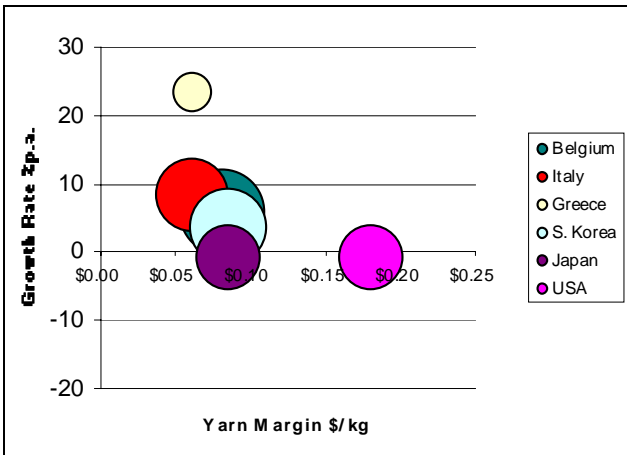


Figure 7. Yarn market analysis.

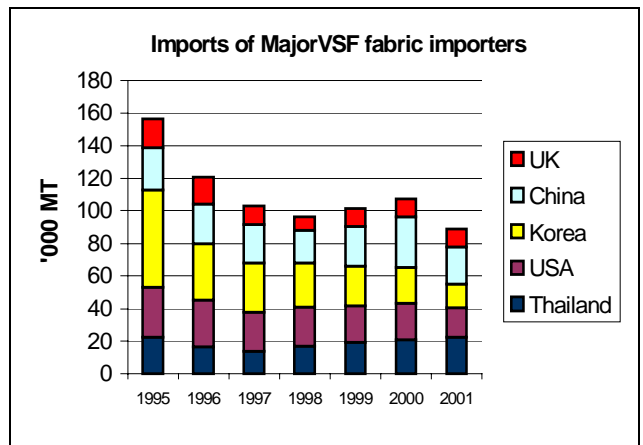


Figure 10. Stagnation in major VSF fabric import markets.

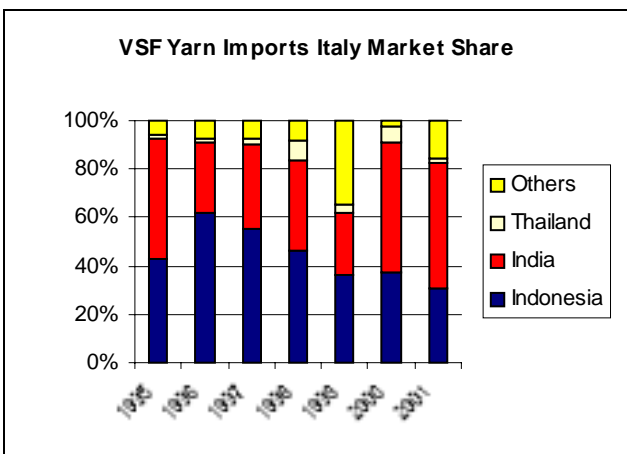


Figure 8. Indonesia is losing share in Italy.

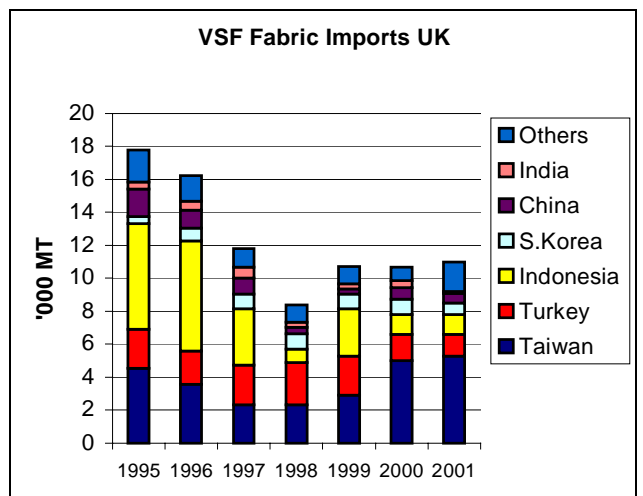
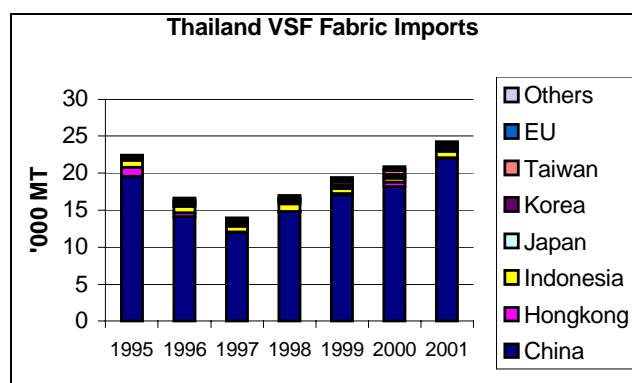


Figure 11. Indonesia has lost market share in the UK VSF fabric market, from 36 % in 1995 to 11 % in 2001.





**Figure 12.** VSF fabric imports into Thailand are dominated by China.

### Strategies for the future

In order to be successful in the future, Indonesian viscose yarn and fabric producers will have to look for new areas of sustainable competitive advantage. With the past paradigms changing rapidly due to regional trade blocks, they will have to systematically look for new strategies by looking at structural advantages, strengths in brands or reputation, business system advantages, internal skills and where their competitors are facing constraints.

### Structural advantages

Indonesian spinning and weaving mills are usually outfitted with +30.000 spindles and +100 looms (A.J.) or +600 shuttle. Advantages stemming from the economies of scale are limited due to the modular structure of the equipment. Any reduction in fixed costs will be marginal with the addition of more equipment since the major overheads are linked to the interest and depreciation on the invested capital. The high concentration of spinning and weaving mills in Central and West Java give companies the advantage of low transportation costs and close relationships with their customers. Conversely, in export markets, Indonesian exporters are handicapped by the relatively high freight costs compared to other Asian countries. With 3 modern viscose fiber plants in Indonesia, there is ample supply of high-quality viscose fibers to support the downstream industries. This is reflected in the relatively high consumption of viscose fibers in Indonesia, 12 %, vs. the world average of 4 %.

The Indonesian government supports most textile producers with low import duties on raw materials. In the ASEAN markets, Indonesian producers also enjoy duty advantages compared to other countries outside the trade zone.

### Business system and reputation advantages

Indonesian yarns are able to match the quality levels in Europe and USA. Fabrics, however, are mainly deemed suitable for printing. The fact that over 90 % of fabric exports are greige fabrics indicates that Indonesian dyeing and finishing capacities need to be improved to become more competitive in the global markets.

Extremely low labor costs and subsidized power costs provide Indonesian producers with an advantage in variable manufacturing costs. Yarn spinning equipment is usually world-class and relatively new. Shuttle weaving capacity is large and low-cost but air-jet weaving is proving to be increasingly uncompetitive.

In the field of product marketing, the Indonesian producers depend to a high degree upon traders in export markets. In contrast, a strong network of close supplier-customer relationships supports sales in the local market. The product focus in Indonesia is mainly on commodity yarns and fabrics, which are easy to sell. The limited development of new products by Indonesian producers is due mainly to their past focus on economies of scale as a competitive advantage.

### Constraints on competitors

The Indian export subsidies on viscose yarns have helped them penetrate the European and Korean markets. This is actually a constraint on Indonesian spinners. There is hope that Europe will impose anti-dumping duties on imported yarn, which should not affect Indonesian spinners.

Turkey recently imposed anti-dumping duties on Chinese viscose fabrics. This has created an opportunity for Indonesian weavers if they can adapt to the constructions and fabric widths needed in the market.

Taiwanese viscose fabric producers are strong in innovation but the industry is shrinking. Luring Taiwanese fabric finishers to Indonesia should be

a top priority. This will bring the technology needed to improve the competitiveness of Indonesian viscose fabrics.

Indonesia remains at a large disadvantage compared to other Asian countries with respect to viscose yarn and fabric exports to the USA. This is due to the small quotas available to Indonesian producers. More lobbying needs to be done to gain equal access considering the size of the Indonesian viscose textile industry.

### **Conclusions**

The USA and Europe are switching their garment and textile sourcing to regional suppliers. This will make continued growth in exports from Asia more difficult. Indonesian VSF yarn exports are still growing at a faster rate than the total import market. Indian and Thai

yarns are becoming threats to Indonesian yarn exporters in key markets like Italy and Korea. There is some potential for VSF fabric exports from Indonesia. The strategy must utilize the competitiveness of the shuttle loom capacity in Central Java as well as develop more sophisticated fabric finishing capacity to compete with Turkey and Taiwan. More focus must also be given to the Indonesian, Asian and non-quota markets for textiles. In the future, local and regional markets will give better margins and more stability to Indonesian producers as regional trade pacts make exports less attractive.

## CELLULOSE IS MUCH MORE THAN A CHEMICAL

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**Cellulose is the basic substance of life. It is the product of a constant circuit comprising water, carbon dioxide and energy. And for this reason alone – as long as there is life on**

**this planet – it is an ideal substance for materials for human use.**

**Keywords:** cellulose, viscose process, fibers

Cellulose occurs – as one might expect from nature – more or less in association with other substances and in a non-uniform appearance. This is acceptable for a lot of applications, but not for modern chemistry, which requires chemicals to be used as pure and as uniform as possible. For this reason it was a happy circumstance that cotton linters were used to develop „artificial silk“ according to the Nitro and Cupro processes. In the viscose process introduced later for the production of cellulosic man-made fibers of wooden pulp, the rules of chemistry, today considered a matter of course – *i.e.* the purity and uniformity of the chemicals used – were elaborated step by step. This included determining limit values for impurities and agreements regarding the average rate of polymerization of pulp (DP), whereby incidentally the DP is only a nominal size, which cannot be recorded with any degree of exactitude. Likewise the condition of the pulp – sheets, rolls or pulverized – was determined as far as possible by a whole series of test processes within relatively narrow limits. In this way it was possible and it still is possible to optimize the procedure without reaching the reactivity of the cellulose, which the existing hydroxyl groups lead us to expect. Also additives help only marginally to influence the reaction process. Generally, it is still the case that chemical implementations in the viscose process are both time-consuming and problematic.

With regard to regenerating the cellulose in fiber form, on the other hand, lots of progress has been made in terms of designing the fiber properties – such as the titer, cross-section, fiber surface, crimping, tenacity, elongation, performance

capacity and dyeing behavior. Moreover, for a long time substances have been added to viscose, which convey special properties to the fibers, *e. g.*, a more or less pronounced brightness, color, flame-retardation, an X-ray contrasting effect, changes in the dyeing behavior and special adsorption properties for hygiene and medical applications. When it comes to additives, viscose offers a wide range of possibilities since there are lots of interesting substances for the market, which resist alkaline and acidic production conditions. A high temperature resistance - as with the production of melt-spun fibers - is not necessary.

To sum up it, can be stated that the viscose process offers lots of interesting possibilities. It is, however, necessary to solve the ecological and economic problems, which are already important today and will gain importance. In this field Lenzing has – in my opinion successfully - conducted admirable research and development work and developed solutions which are futuristic.

### **So what is it all about now?**

In the course of the last decades the work carried out in an uninterrupted fashion to solve those problems, which still exist with regard to the production of viscose fibers – unquestionably smaller but still around –, has furnished a wealth of practical experience since it was possible to compare the derivative process with the solvent process in big scale production. In this respect it has been seen – and that is state of the art of engineering – that both of these processes and

their products have disadvantages and advantages. If one concentrates on what is decisive, then the *viscose process* has the advantage of being able to produce a whole range of fiber types, which can largely be processed in their respective applications without any difficulty and turned into valuable finished articles. In line with our knowledge to date this is also true of other derivative processes.

These processes also force us to „come to terms“ with the „derivation agents“, which is not so easy and presents a number of special problems in the viscose process. In addition, the derivative solution contains a relatively small amount of cellulose so that relatively large volumes have to be moved, tempered and cleaned, which takes a lot of effort, and influences the regeneration process of the cellulose from the viscose solutions.

On balance, viscose is an interesting fiber for the textile world – producing it, however, involves a number of problems from an economic and ecological point of view.

### What has to be done?

The realization that the number of hydroxyl groups in the cellulose molecule allows us to expect a higher reactivity than was observed encourages chemists to make these hydroxyl groups more accessible – to “activate” them, whatever that might mean. As a result the reaction speed will increase and will probably be less problematic, producing a series of consequences for the process.

Is this only wishful thinking or are there still some possible ways of „activating“ the cellulose molecule? We know of course that the irradiation of eucalyptus pulp of one manufacturer with electrons represents a good approach, which is worthwhile to follow. Even if there is still no unanimous opinion about the causes of the effects determined and the transfer of this to other types of pulp, this procedure is too promising not to be paid further attention to.

What have previous tests revealed in unambiguous terms:

- The amount of NaOH and CS<sub>2</sub> used can be reduced and the cellulose concentration in the viscose can be increased. The low

particle counts in the viscose alleviate filtration and improve the spinning behavior.

- By adapting the spin baths and the after-treatment, the properties desired can be obtained for standard fibers.
- A reduction in the operating time for the pulp used is possible.
- Moreover, it can be seen that the potential for improvement, when compared with the classical procedure, has not been exhausted so far.

Therefore, the results worked out point all in the right direction: an improvement in the ecological and economic aspects of the viscose process.

The facts illustrated do not just demand further development, but also require research to fully clarify what interrelations there are to allow a universal application, and perhaps even to determine what the effects of this might be.

All that remains is to consider whether the regeneration of viscose - as was common until now - will take place in the future from the bottom to the top, or - as in the case of the Cupro process - from the top down. This would avoid the „bathing trunks battle“, which limits the spinning speed. This is a technical problem which can be solved relatively simply with the knowledge available.

To summarize, it can be said that the viscose process still has a great deal of potential for improvement. In the truest sense of the meaning it would, therefore, appear to be beneficial to make use of the approaches already established and find answers to the questions already formulated which are as follows:

- to activate the reaction ability of the cellulose,
- to increase the spinning speed, and
- to continue closing off production towards a closed circuit process.

### Solvent processes

A general reflection of the situation leads us to the conclusion that the regeneration of cellulose from derivatives must contain more chemical and technical possibilities to control the process than a solvent process. Nevertheless, the question arises whether there are other plausible ways, in

which the targeted goal can be more easily reached than done to date, *i.e.* the production of fibers without the tendency to fibrillate. This would make it possible to considerably extend the application range of Lyocell fibers, however without obtaining the variety of viscose fiber types.

To sum up, it can be said with certainty that solvent processes also have development potential; however, the fibers produced according to these processes cannot be so readily modified as we are used to do with those from the viscose process. However, since cellulose is available practically in unlimited quantities and a rising quantity of fibers is needed, it is worth making a research effort in both fields – the derivative and the solvent processes.

### **Are there other tasks for R&D in the field of cellulosic man-made fibers?**

I think so; they are developing along with the market and with the increasing importance of ecology – even for fiber products and their applications.

On the one hand, the market place is demanding large quantities of fibers of one type and on the other hand smaller to small quantities of specialty fibers. In my opinion development work did justice to the large lots of the past decades in an excellent manner. Today the productivity of the plants has reached an impressive level and still appears to have potential for further increase.

On the other hand, I believe that the development work in smaller, but more flexible plants has been left behind. There is a demand for it in the market, which will grow since classical dyeing and finishing of textiles is increasingly running into problems, which include the environment and the cost and fastness values, to name but a few.

However, solving this task will not merely mean developing flexible spinning machines for small quantities, but also a system that organizes the use of the right additives in accordance with their type and quantity. In most cases it certainly makes no sense to spin special fibers to be kept in stock or to let customers wait for weeks on an order being fulfilled. An order, *e. g.* about a spun-dyed type, has to be dealt with to the

customer's satisfaction within a few days, at most 2 – 3 weeks. There is not longer a need to prove that this can be accomplished with the proper organization and necessary machinery adaptations. LENZING SXS-Technik is here an excellent example. We can add the companies' willingness to produce large quantities. Even the subject of the „cost“ and passing this on to the customer within the textile pipeline can be solved: the simplest way is naturally in textile companies, which have all phases of the textile process.

It goes without saying that spin dyeing is unlikely to replace classical dyeing in the fashion area – that is, moreover, certainly not the goal – but it can, where this is desired, raise the color fastness levels of textiles to a higher level. This applies for example to cotton textiles with which these kinds of spun-dyed viscose fibers are blended.

The fact that the manufacturer of special fibers, when signing large-scale contracts on natural white, has normally good opportunities is of course a beneficial side effect of the effort he has undertaken – with which money can, as such, be earned. The fact that the equipment needed for this can also be used to produce special fibers needs not be given any particular mention.

I see another task for the engineer trying to develop applications for cellulosic man-made fibers in the field of spun-bond materials where it is desirable to use degradable fibers when producing various hygiene and medical textiles. What happens to these after their use would then no longer represent a problem. Naturally, more lightweight spun-bond materials of cellulosic man-made fibers would be a new addition to the market. They do, however, involve problems, even though their advantage – the degradability – would seem to guarantee real chances, particularly since they can also be suitably modified.

At the end of this paper, let us come back to a dream of all cellulose chemists, namely to increase the maximum tensile strength even further. If one evaluates the pertinent tests carried out to date to produce extremely strong fibers from cellulose, then one finds no clear approach, particularly if one also adds synthetic fibers and the possible costs of production to these considerations. What would, however,

happen, if we transferred the wide-ranging knowledge we have concerning composites to fibers? Today it is natural to use molecules with the longest chains possible to produce high-strength fibers and to orientate these in the fiber direction as well as one can. To this end, corresponding starting substances are used. With all kinds of composites, fiber-reinforced plastics, the matrix and the reinforcement fibers are not joined together until the composites are produced. If this production process is transferred to the production of fibers then the long-chain molecules – for the reinforcement of individual fibers – should only be added shortly

before the regeneration of the fibers like other additives. The only logical thing to do is to extend this idea to short fibers of cellulose and other polymers. This would pave the way to two-component fibers with a cellulose matrix whereby the cellulose would guarantee the good adherence to other substances for which it is known. This is undoubtedly a vision but it is not utopia – a thought that shows what cellulose “still has to offer”.

It is up to us to develop ideas, to examine these and turn them into reality. He, who rests, is lost.

## VISCOSTAR® - A STAR-SHAPED VISCOSE FIBER FOR IMPROVED ABSORBENCY

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For many absorbent nonwoven products, such as tampons, viscose is the dominating cellulosic fiber. As tampon manufacturers aim at continuously improving the performance of their products, a new approach was taken to develop a viscose fiber especially designed for this particular end-use. The traditional parameters used to measure the absorbency of fibers (water retention and imbibition) turned out to be insufficient to characterize the absorbency of tampons. Novel lab methods for manufacturing and testing of tampon-shaped plugs had to be introduced and syngina absorbency was selected as the lead parameter for fiber development.

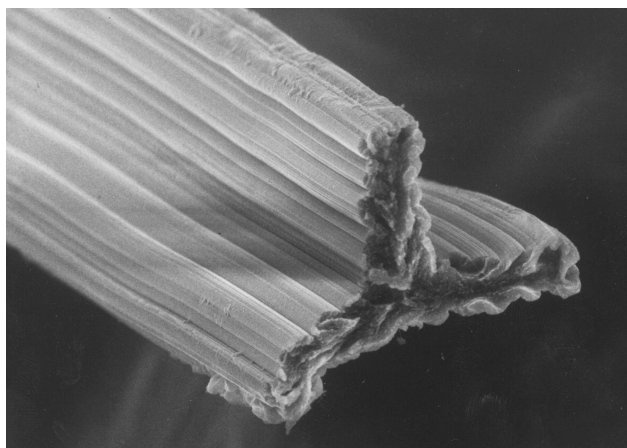
In a comparative study, a viscose fiber with a trilobal cross section seemed to be the best option. In order to achieve maximum

syngina absorbency, the geometry of the fiber cross section had to be defined and a spinneret had to be designed providing good spinnability, a consistent shape of the fiber cross section and high spinneret lifetime. For the first time a computer-aided simulation of the fluid dynamics in viscose fiber spinning was used to support the spinneret design process.

By a systematic investigation of the influence of certain process parameters on tampon absorbency, the performance profile of Viscostar® - the new star-shaped viscose fiber - was optimized. Upscaling from pilot plant scale into commercial production has been successfully completed. Viscostar® is a totally chlorine free viscose fiber, which meets the highest product safety standards and improves the absorbency of traditional tampons from viscose/cotton-blends significantly.

### Introduction

Viscostar® is a viscose fiber with a star-shaped cross section, which was designed to improve the absorbency of nonwoven products, especially of tampons.



Cross section of Viscostar®.

Profiled viscose fibers and filaments have already been known for many years, so this paper will not deal so much with the fiber itself, but concentrate on the new approaches, which have been taken to better understand the interactions between production parameters and fiber properties on the one hand and performance, especially absorbency of the final product, on the other hand, and will present some new tools and models which had to be developed for this purpose.

Unlike in textile applications, viscose is the dominating cellulosic fiber in nonwovens, because of its superiority in absorbency and purity and the tailor-made physical properties. Nonwovens are a rather stable and constantly growing market, and one of the most sensitive nonwoven products are tampons. Today, about 75% of the fibers used for tampons worldwide are already viscose fibers, and cotton is going to be phased out.

Like most other manufacturers of consumer goods, tampon producers are continuously improving their products by either increasing the performance or reducing costs of their products or even both. For tampons, this means to achieve higher absorbency with the same amount of fiber or to maintain a certain level of absorbency with less fiber material, thus improving comfort and reducing costs.

In response to the needs of tampon manufacturers, Lenzing R&D started a research project to develop tailor-made tampon fibers with improved absorbency.

The first approach was quite simple: if you want to have a tampon with improved absorbency, you have to take a fiber with improved absorbency. We started to explore the technical feasibility of making absorbent fibers by various physical and chemical modifications and to investigate the performance of such fibers in tampons, see Figure 1.

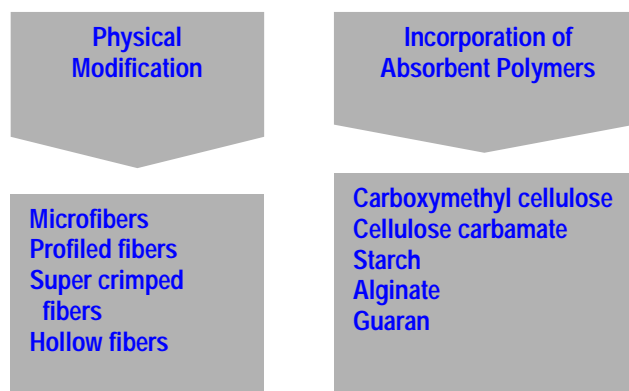


Figure 1.

## Absorbency of fibers

The parameters traditionally used to characterize the absorbency of cellulosic fibers are water retention and water imbibition.

While water retention<sup>1</sup> measures the amount of liquid retained by swelling inside the fiber after removing the excess liquid in a centrifuge, water imbibition<sup>2</sup> measures the water holding capacity of a loose bundle of fibers under gravitational forces.

A major question was, which of these parameters should be selected as the lead parameter to

achieve maximum tampon absorbency. In order to find an answer, prototype fibers with a wide variation in absorbent properties were manufactured and processed into tampons, thus investigating the correlation between fiber absorbency and tampon absorbency. The range for water retention of the prototype fibers investigated in this study was between 40 to 140%, for water imbibition between 21 to 28 g/g. Looking at the outcome of this exercise, we found that the correlation between water imbibition of the fibers and tampon absorbency was extremely poor. Fibers with a high water imbibition value, such as cotton or a physically modified viscose fiber codenamed "Hydrophil B", performed less well than the trilobal fiber Viscose TC or a chemically modified viscose fiber containing guaran, which was called "Hydrophil G" (Figure 2).

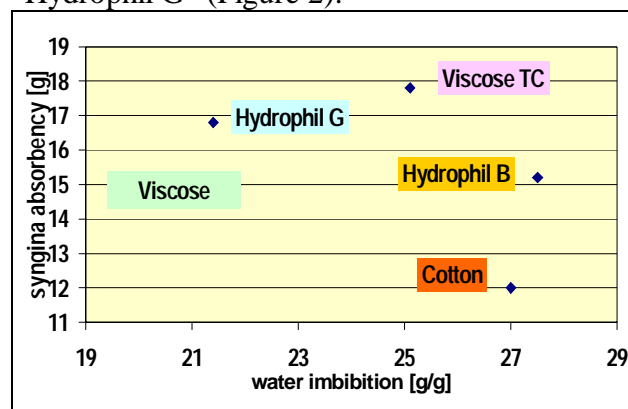


Figure 2.

The correlation for the water retention value looks better, but a significant increase in water retention did not lead to an improvement in tampon absorbency as can be seen by comparison of Hydrophil G and Viscose TC (Figure 3).

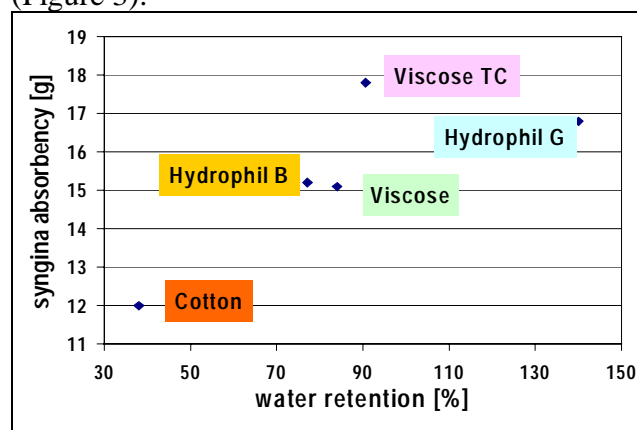


Figure 3.

<sup>1</sup> determined according to DIN 53814

<sup>2</sup> determined according to European Pharmacopoeia 4 01/2002:0034



Parameter	Lenzing	ERT 350.0-02
<b>Test fluid:</b>	deionised water	10 g/l NaCl soln. 0.5 g/l acid fuchsin
<b>Position of Syngina chamber:</b>	vertical	30° to vertical
<b>Hydrostatic Pressure:</b>	180 mm	180 +/-10 mm
<b>Temperature:</b>	room temp.	27 °C
<b>Addition of fluid:</b>	25 ml at once	50 ml/ hr
<b>End point:</b>	after 3 min.	leakage

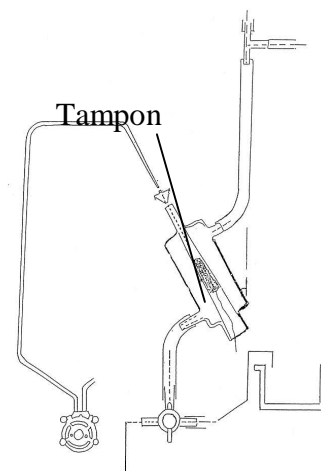


Table 1.

So the conclusion was, that none of the parameters used to characterize fiber absorbency was suitable as the lead parameter to maximize tampon absorbency and that a fiber with trilobal cross section seemed to be the best choice. It also showed, that other - at that time unidentified - parameters than fiber absorbency have a significant influence on tampon absorbency and that we had to take the absorbency of the final product as the lead parameter for our fiber developments.

### Tampon absorbency

Tampon absorbency is measured by application of the so called Syngina Test. The absorbency of a tampon is tested under simulated „real-life“ conditions at a certain hydrostatic pressure.

As no international standard was available at that time we developed our own Syngina Test. In the meantime a European standard test has been issued by Edana<sup>3</sup>. The Lenzing Syngina Test, is a simplified version of this Edana test, see Table 1.

At that stage of development we had available the tools to manufacture new fibers in pilot plant stage and to assess the absorbency of tampons. However, we were not able to process small quantities of fibers into tampons for testing Syngina absorbency.

In order to do this in cooperation with tampon manufacturers, at least 30 kg of fiber were necessary, and in order to provide 30 kg of fiber material we had to run a short production trial,

which forced us to develop a new technology to the extent necessary for a production run.

Under these circumstances, a complete development cycle with a new fiber took 6-12 months, and this was unacceptable for an efficient R&D work. Consequently, there was a clear demand to turn the wheel of innovation much faster.

A lab method was developed for processing a certain amount of staple fiber into a card sliver, compacting and rolling the sliver to form a cylinder, putting the sample into a mechanical press, forming a plug with the same shape, volume and fiber orientation as a digital tampon and measuring the absorbency of the plug in a Syngina Test (Figure 4).

With this equipment it was possible to reduce cycle time down to a few days and it was easy to get a quick feedback from small fiber samples. By comparison of results obtained from plugs and commercial tampons, which were manufactured from the same fiber materials, we were able to validate our method and to confirm the good correlation.

Now all the necessary prerequisites were in place for an efficient design of a tailor-made tampon fiber, and we were ready to start our Viscostar<sup>®</sup> project.

<sup>3</sup> ERT 350.0-02

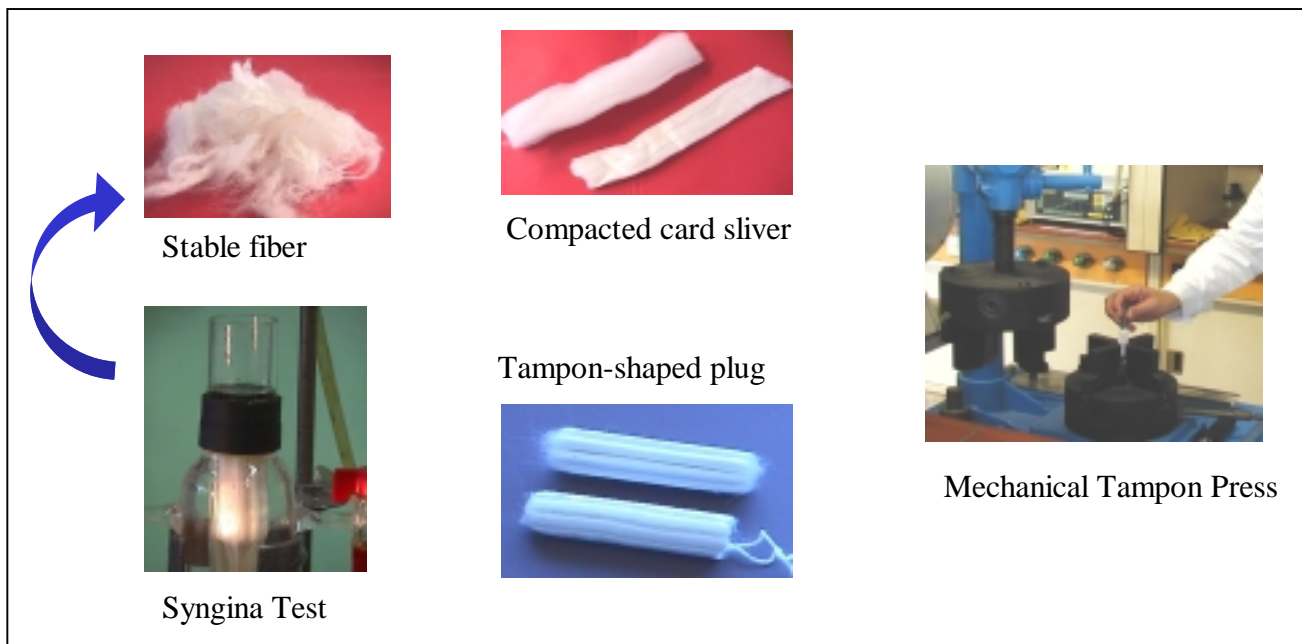


Figure 4.

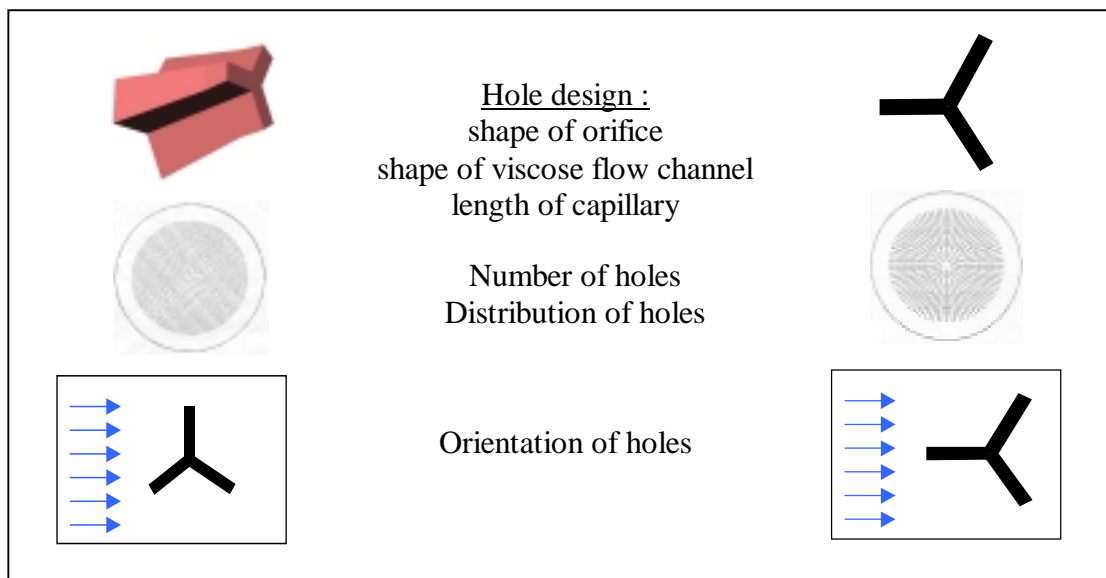


Figure 5.

## The Viscostar® Project

### Spinneret design

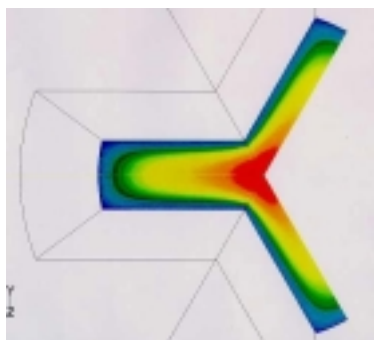
The heart of the process for making trilobal fibers is the spinneret. The design of a trilobal spinneret had to take into account:

- a well-shaped and consistent fiber cross section
- good spinnability and high productivity
- low sensitivity to process variations
- and high spinneret lifetime without clogging

Compared to traditional spinnerets with circular holes, profiled spinnerets have much more design parameters.

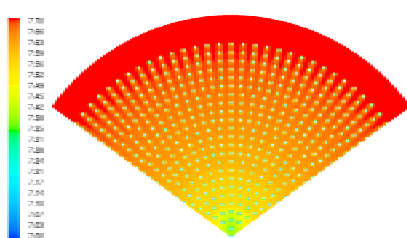
The length-to-width ratio of the limbs of the spinneret is of critical importance for the aspect ratio of the limbs of the fiber, but also the shape of the viscose flow channel and the length of the capillary have an influence on the fiber cross section. The number of the holes per unit area, their distribution and their orientation towards the radial flow of the spin bath are important for spinnability and productivity of the trilobal spinneret (Figure 5).

Together with an Austrian university, a model for computer simulation of the viscose flow inside the spinneret was developed. In diagram 1 different flow rates in a section of the trilobal spinneret are visualized by a grey-scale code. We observe a high flow rate in the inner zone, whereas the outer zone with a low viscose flow rate is critical with regard to coagulation and partial clogging.

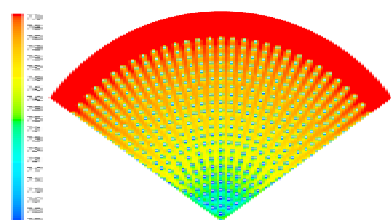


**Diagram 1.**

Our spinneret design targeted achieving a good uniformity of the viscose flow, but for a stable spinning process uniform spin bath flow and acid distribution are also most important. So a computer model was developed, which allowed us to combine the chemistry of the regeneration process with the fluid dynamics of wet spinning and enabled us to simulate the acid distribution across the spinneret surface for various designs.



**Diagram 2.**



**Diagram 3.**

Diagram 2 shows the acid distribution very close to the spinneret surface, diagram 3 in a

distance of 11 mm from the surface. The lower zone shows the drop in acid concentration in the center of the spinneret. Computer simulation gave us a much better understanding of the critical design parameters of a spinneret, but the theoretical results had to be validated by spinning trials on our pilot plant.

### *Pilot plant spinning trials*

The viscose pilot plant of Lenzing R&D, manufactured by Lenzing Technik is designed for spinning of about 1 kg viscose fibers per day. The modular equipment is downscaled from industrial installations and furnished with the same type of process control system.

About 20 different spinneret designs were tested in this pilot plant. Small variations of the aspect ratio of a trilobal spinneret can have a significant influence on the shape of the fiber cross-section and also on syngina absorbency.

Experience with circular hole spinnerets shows, that a certain hole diameter of e.g. 90  $\mu\text{m}$  is suitable for spinning of fibers in the range from 2,8 to 5,6 dtex without any significant influence on fiber properties. Trilobal spinnerets however can only be used in a relatively narrow window of titer. Outside this window the shape of the cross section changes significantly.

Once the decision for a certain design of the trilobal spinneret had been made, the process conditions had to be optimized to achieve maximum syngina absorbency. In order to reduce the number of trials, experimental design with a limited number of parameters was used (Figure 6).

Surprisingly, the type of pulp can have a significant influence on syngina absorbency: prehydrolyzed kraft pulps seem to perform better than sulphite pulps (Figure 7).

The addition of a viscose modifier, e.g. PEG 1500 has a positive influence on syngina absorbency (Figure 8).

Scaling up from pilot plant to bulk production was performed step by step.

Depending on pulp quality, absorbency slightly declines with increase of production speed (Figure 9).

Finally, in a 110-hours production run it could be proved, that Viscostar can be produced in consistent quality without a frequent change of spinnerets.

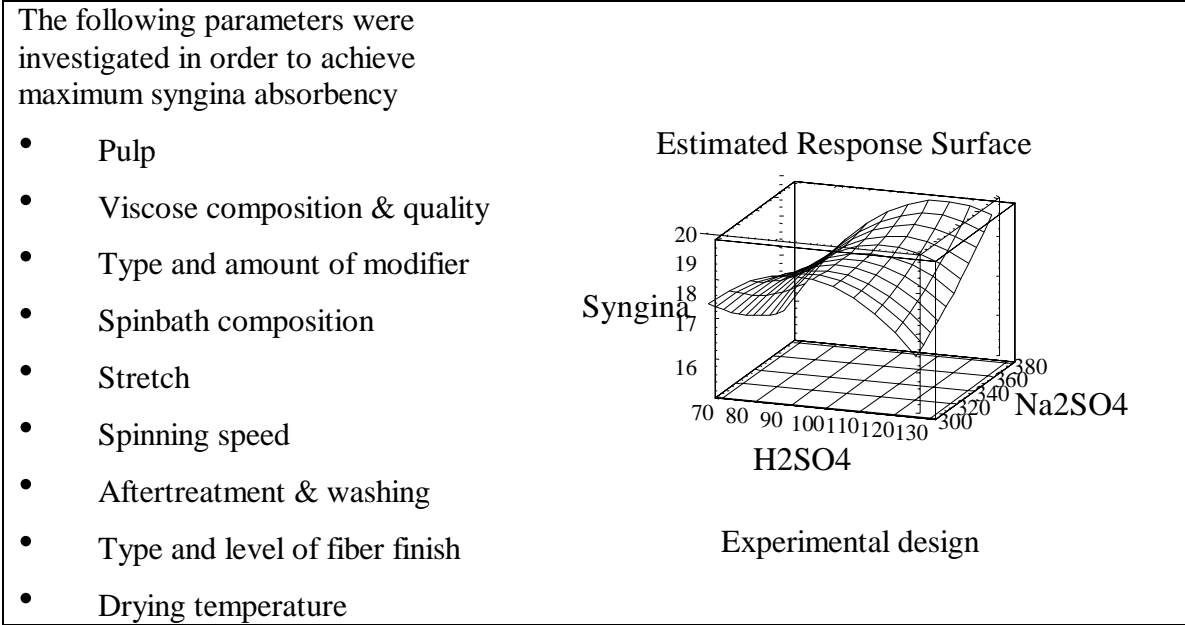


Figure 6.

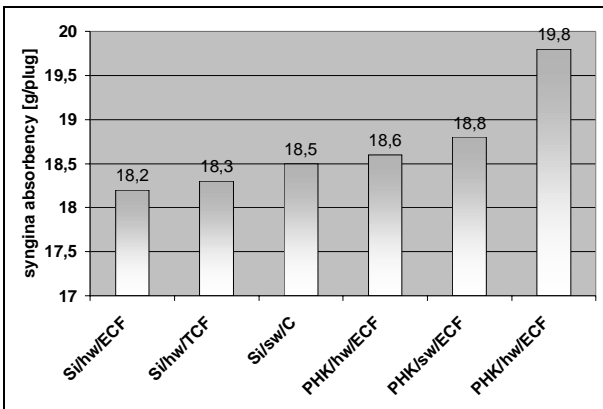


Figure 7. Si = sulphite; PHK = prehydrolyzed kraft; hw= hardwood; sw= softwood; ECF= elementary chlorine free; C= chlorine bleached; TCF= totally chlorine free.

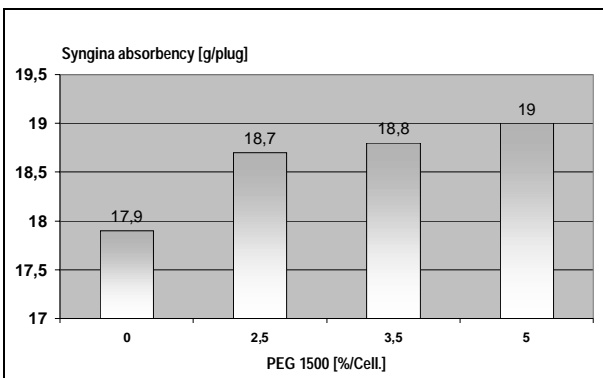


Figure 8. Effect of adding a viscose modifier.

The profile of Viscostar®

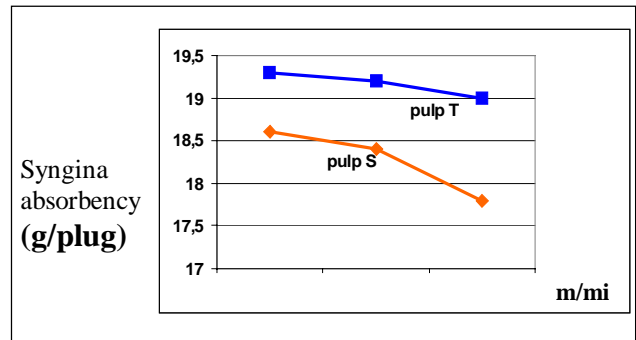


Figure 9. Absorbency vs. increase of production speed.

Compared to regular viscose Viscostar® is characterized by a higher titer, the same staple length and tenacity, a lower elongation, a higher water imbibition at the same level of water retention, of course a higher Syngina absorbency, and a higher bulkiness. The finish level is a little bit higher, PEG content is below the limit of detection, and the fiber is bleached totally chlorine free [tab.2].

## Summary

What we have experienced in this project is, that enhanced fiber absorbency does not necessarily lead to improved tampon absorbency. For this reason, the absorbency of the final product - the tampon - and not the absorbency of the fiber was selected as the lead parameter for the development of Viscostar<sup>®</sup>.

Novel lab methods for manufacturing and testing of tampon-shaped plugs had to be introduced.

For the first time a computer-aided simulation of the fluid dynamics in viscose fiber spinning has been used to support the spinneret design process. Viscostar<sup>®</sup> is a star-shaped TCF

viscose fiber, which meets the highest product safety standards and improves the absorbency of traditional tampons from viscose-cotton-blends significantly. Compared to tampons made of 100% cotton the absorbency of Viscostar<sup>®</sup> tampons is up to 50% higher.

## Acknowledgement

This paper is based on the research work performed by the Lenzing Viscostar team and I would like to thank especially my co-workers Susanna Schiemer, Helmut Weißböck, Heinrich Schmidt and Robert Kickingner for their valuable contributions and their excellent work.



<b>titer [dtex]</b>	3.3 +/-0.1	2.8
<b>staple length [mm]</b>	30	30
<b>tenacity cond. [cN/tex]</b>	22	22
<b>elongation cond. [%]</b>	17	21
<b>water imbibition [g/g]</b>	25.5	21.5
<b>water retention [%]</b>	87	85
<b>rel. syngina absorbency [%]</b>	117	100
<b>rel. bulkiness [%]</b>	140	100
<b>finish [% ] (EtOH extr.)</b>	0.06	0.06
<b>PEG [%]</b>	n.d.	n.d.
<b>TCF</b>	✓	✓

Table 2.

## RAINBOW: A NOVEL VISCOSE FIBER FOR PES BLENDS INNOVATIONS IN DYEING TECHNOLOGY

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Blends of Viscose and PES are widely used in the textile industry, but the traditional dyeing process is complex as a two-step procedure is required. Using the Rainbow fiber, the fabric can be dyed in a single step at low pH without addition of salt requiring only one rinsing step and achieving a very high degree of dye bath exhaustion. Thus, dyeing time is reduced by 50-65% giving the dyehouse manager the opportunity to double or triple productivity. An additional benefit is the reduced consumption of energy, (waste) water and salt. This unique combination of properties has been realized by incorporation of a cationic

polymer into the viscose spinning dope, thus achieving permanent modification. Suitable dyeing procedures have been developed in cooperation with DyStar. By an appropriate selection of DyStar direct or metal complex dyes, a light fastness similar to conventional viscose has been achieved while all other fastness properties remain equivalent to viscose fibers.

**Keywords:** cationization, viscose fiber, incorporation, PES-blends, dyeing, one-step

### Introduction

During the last 50 years worldwide fiber production has increased fivefold to some 52 million tons per year due to an increase in population and a higher per capita consumption. This huge increase could only be covered by synthetic fibers which reached a quantity of about 27 million tons per year with the most prominent contribution from polyester fibers (19 million t/a), see Figure 1.

Worldwide fibre consumption 2000 (%); total 52 million tons

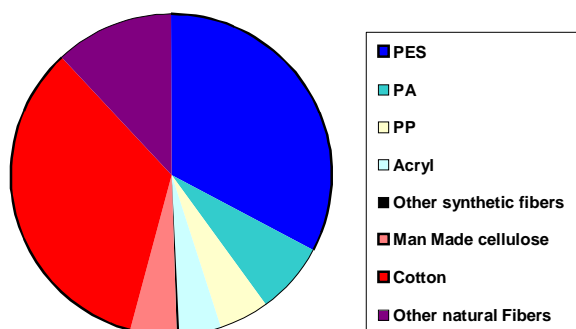


Figure 1. Fiber consumption in the year 2000.

In the same period of time the production of cotton increased about twofold to approximately 20 million tons per year, while the cultivated area remained constant [1]. Higher output has been achieved by herbicides, agrochemicals and elaborated irrigation systems. The utmost limit of production has been reached by now as cultivated area will most like not be increased [2] or even be reduced due to shortages in water supply, erosion or the necessity for food production. Cotton plants with higher productivity are also not feasible [3].

Till 2010 fiber demand will increase even further to some 65 million tons per year due to a population increase and an increase in per capita demand. The above outlined reasons suggest that this demand can only be covered by synthetic fibers. But as people opt for fabrics with a high comfort when wearing and easy handling when washing, polyester-viscose blends can be the material of the future.

Polyester fibers offer excellent textile properties. High tenacity (dry and wet) results in good mechanical properties and durability. Furthermore, polyester shows good dimensional

stability at a reasonable price. Problems can be found in wear comfort, as polyester is a hydrophobic fiber and thus cannot control humidity. The material feels wet on the skin, which results in a sensation of low comfort. Polyester microfibers used in sport applications transport humidity via capillarity, which works well at high “sweat levels” but has only limited applicability in “normal life”.

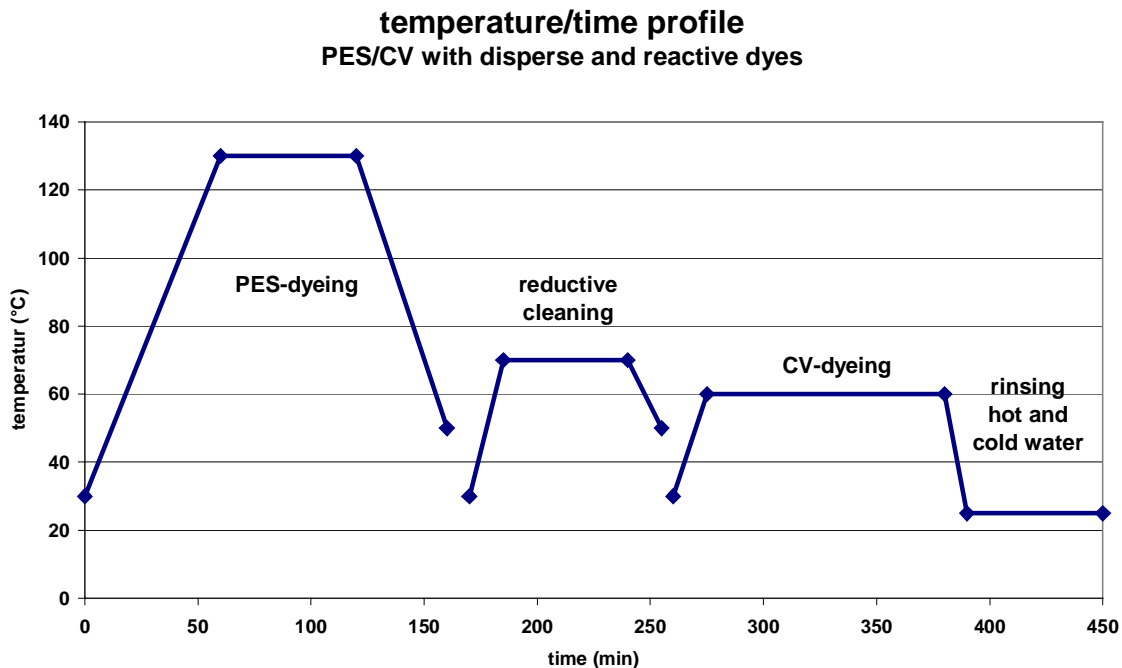
Cellulosic fibers, on the contrary, show water retention of 40% to 80%, and can thus easily control humidity. The fiber feels dry and comfortable on the skin. In combination with the soft handle cellulosic fibers offer excellent wearability.

The profiles of these two fibers suggest that a combination of both fibers should result in an optimum for textile applications. These somewhat theoretical considerations are verified by the market. About 5 million tons of polyester viscose blends are processed per year, which makes this fiber blend the most important on the market. As we are facing a significantly increased fiber demand, blends of polyester and viscose should also increase in quantity, assuming that the consumer consistently wishes high wear comfort. It can be estimated that about

8 million tons of polyester-viscose blends will be processed by the year 2010.

Dyeing of polyester-viscose blends (yarns and fabrics) is a very complex process (Figure 2). The blend requires a very high input of labor, when dark shades are to be dyed at high quality. The reason can be found in the very different dyeing procedures of both fibers. Polyester is usually dyed with dispersion dyestuffs at 130 °C and pH 4.5 to 6 while cellulosics are dyed using reactive dyes at 60 °C, pH 6 to 10 and a high dosage of salt. Here, not covalently bound dyestuff has to be removed by soaping and/or washing. This requires that the single fibers have to be dyed one after the other in blends of polyester and viscose. The whole process has a duration of 10 to 12 hours, which can become even longer if corrections have to be made. Cellulosics could also be dyed by direct dyes under polyester conditions, which results in fair quality only at light shades.

Lenzing has developed a new cationized viscose fiber dubbed “Rainbow”, facilitating the dyeing procedure and drastically reducing time consumption, whereby environmental compatibility could be improved significantly.



**Figure 2.** Time / temperature profile of a conventional polyester-viscose blend.

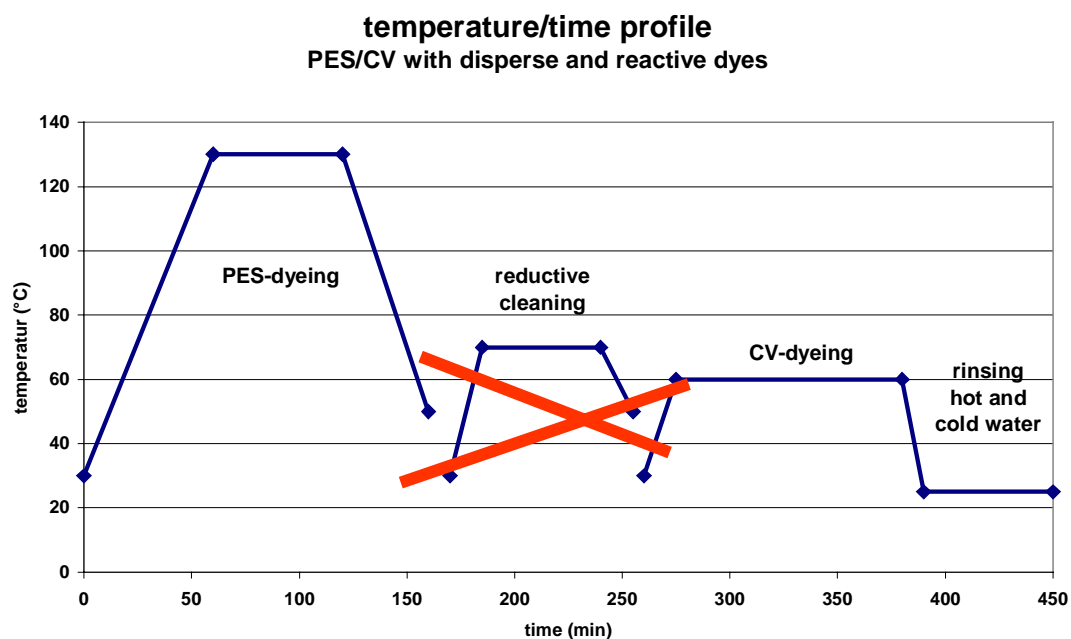
## Methods

The viscose dope has been cationized by incorporation of a cationic polymer using standard laboratory equipment, and has been spun into fibers using a standard pilot spinning line. Fiber after-treatment has been done at laboratory scale. Samples have been dyed using Mathis laboratory equipment. Fastness properties have been tested according to international standards. Colorimetric measurements have been

performed on a Minolta Spectrophotometer CM-508/DA.

## Results

Lenzing intended to develop a viscose fiber, which can be dyed under polyester conditions, thus significantly reducing dyeing time of polyester-viscose blends. This fiber development has been named “Rainbow”. In Figure 3, the potential timesavings are indicated.



**Figure 3.** Time / temperature profile of a Rainbow polyester blend.

This ambitious goal has been reached by cationization of the viscose dope before fiber spinning. A cationic polymer has been incorporated in the viscose spinning dope and the fiber has been spun by a standard viscose spinning process. As the cationic polymer is incorporated into the fiber, cationization is permanent, thus cationic charge cannot be washed off during textile processing. Usual textile processes or reducing and oxidizing agents do not affect the charge, there are no limitations at elevated temperatures (*e.g.*, 180°C for 60 s), and cationic charge is constant over a wide pH range (pH 5-13).

The cationic charge is distributed homogeneously over the diameter of the fiber. Thus, no excess charge at the surface can be observed resulting in a very even color distribution during the dyeing process. Looking at fibers cationized during fiber after-treatment, bad leveling can be observed. Figure 4 shows the cationized Rainbow fiber.



**Figure 4.** Cationization in the Rainbow fiber.

Rainbow fibers have the same physical fiber properties (tenacity, water retention, etc.) as usual viscose fibers, except dyeing properties. Rainbow fibers can be dyed at 130°C using direct and metal complex dyes without addition of salt giving fastness properties comparable to reactive dyeing at 60°C.



Color depth has been measured by colorimetric methods (CIELAB; L-values). It was shown that Rainbow has the same color depth as viscose dyed with the double amount of dyestuff or even more. Details can be seen in the upper part of Table 1 (Sirius blue K-CFN and Sirius blue K-CFN). Even at these much higher color depths reached by Rainbow a better wash fastness has been observed. It follows that dye bath exhaustion is also significantly improved. Depending on the dye and intended color depth dye bath exhaustions between 92 % and 99% have been observed. These trends are shown in the upper part of Table 1.

Cationic fibers generally tend to show reduced light fastness. This problem could also be

observed with the Rainbow fiber especially with red shades. This drawback has been solved by an appropriate selection of dyes. A variety of different direct and metal complex dyes is suitable for Rainbow. In collaboration with DyStar an optimal collection of dyes has been selected and tested intensively. These dyes meet the requirement of a light fastness of 4 or higher. Only red shades, like in the case of standard viscose, have a slightly lower light fastness of 3-4, but there are also examples of red dyestuffs with a light fastness of 4. The selection of dyes comprises both direct dyes and metal complex dyes; some examples are listed in Table 1.

	Fastness to rubbing <sup>3</sup>		wash fastness <sup>3</sup>			light-fastness <sup>3</sup>	CIELAB ΔL		
	dry	wet	color	bleed CV	bleed WO		0,5% <sub>1</sub>	1,0% <sub>1</sub>	2,0% <sub>1</sub>
<i>Sirius blue K-CFN; Rainbow</i>	4-5	2-3	4	4	4-5	3	27.5	19.4	13.7
<i>Sirius blue K-CFN; Standard viscose<sup>2</sup></i>	4-5	2-3	3	2	4	7	38.4	29.5	22.5
<i>Sirius brown 3RL; Rainbow</i>	4-5	3	4	3	3	3	44.7	35.3	28.4
<i>Sirius brown 3RL; Standard viscose<sup>2</sup></i>	4-5	3	3-5	3	3	5	58.7	49.8	41.4
<i>Isolan marine S-RL</i>	4-5	3.5	4-5	4.5	4.5	4.5	-	-	-
<i>Isolan yellow K-PRL 200%</i>	4-5	4	4	4-5	4	6	-	-	-
<i>Isolan bordo R 220%</i>	4-5	3	4	4	3	4	-	-	-
<i>Isolan grey K-PBL 200%</i>	4-5	3	4	4-5	3	6	-	-	-

<sup>1</sup> Concentration of dyestuff

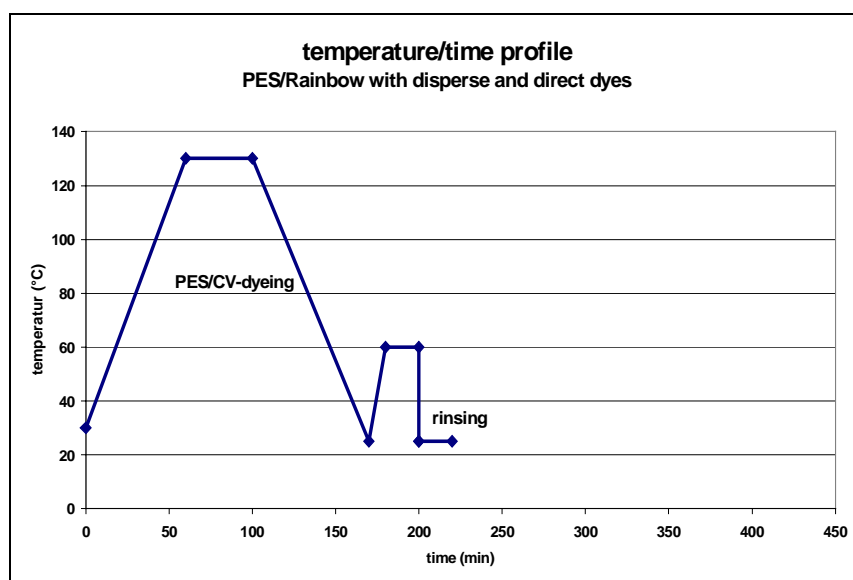
<sup>2</sup> Standard Viscose dyed at 130° with salt (0,5% dyestuff and 10g/l salt; 1,0% dyestuff and 15g/l salt; 2,0% dyestuff and 20g/l salt); Rainbow dyed without salt!

<sup>3</sup> Fastness properties refer to trials with 1,0% dyestuff concentration

**Table 1.** Fastness data and color depth at different dyestuff concentrations of various dyes.

Intensive dyeing trials have shown that polyester-viscose blends can be dyed at polyester conditions at 130°C, pH 5,5 without salt in a one-bath one-step procedure. Promising results have been achieved with both system-blends and intimate-blends. Figure 5 shows the dye time-temperature profile and the timesavings of the Rainbow dyeing process.

It can be seen that an enormous decrease in dyeing time results. Up to 70% of the time formerly needed can be saved. If the dyehouse manager can use this additional time productively, the efficiency or productivity of the dyehouse will increase by the same amount. This should improve the cost structure of the dyehouse significantly, and should help in the every-day dyeing business.



**Figure 5.** The Rainbow dyeing process.

A spin-off of the Rainbow dyeing process is the significantly improved environmental situation. As the whole dyeing procedure is much shorter water consumption and thus wastewater is reduced by 65%. In the Rainbow dyeing process no addition of salt is needed therefore no salt will be in the wastewater. Together with the fact that dye bath exhaustion is much higher than compared to the conventional process with reactive dyes wastewater is also less colored which helps to reduce costs concerning wastewater treatment. Because of the shorter process duration energy costs are also reduce by up to 65%.

## Conclusion

Today, polyester-viscose blends are very important on the market, and this position will become even more prominent when it comes to satisfying the growing demand for textiles, since this blend combines the positive properties of both fibers exemplarily. Unfortunately, the dyeing process is very time consuming and complex. A two-bath exhaustion procedure with dispersion and reactive dyes, each followed by rinsing steps, has to be used, which increases dyeing costs significantly.

With Rainbow, a cationized viscose fiber, the time needed for the dyeing process could be reduced by up to 70%. Thus, polyester-viscose blends can be dyed at significantly reduced costs

in a single step, and dyed fabrics are fully leveled and achieve fastness properties comparable to standard viscose. Rainbow is dyed under polyester conditions (130 °C, pH 5-6) using direct or metal complex dyes. By an appropriate selection of dyes, performed by DyStar, light fastness properties equivalent to standard viscose dyed with reactive dyes were achieved.

Further advantages of Rainbow are the reduced water and wastewater quantities (by 65 %) and reduced energy costs (by 65 %) per kilogram of dyed fabric. There is no salt, and because of higher dye bath exhaustion and thus lower amounts of required dyestuff the amounts of dyestuff in the wastewater are reduced. The laboratory development of Rainbow is finished; scale-up of the production line is currently performed. Various trials have proved that the theoretical improvements can be achieved in the dyehouse. Now, additional tests have been started before the introduction of the Rainbow fiber.

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# LENZING LYOCCELL: POTENTIALE EINER NEUEN FASERGENERATION

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Ein paar Jahre nach der Inbetriebnahme der ersten kommerziellen Produktionsanlagen, in denen die über mehr als ein Jahrzehnt entwickelte NMMO-Technologie für die Herstellung von Lyocell-Fasern genutzt wird, beginnt sich nun das hohe Potential dieser neuen Generation cellulosischer Fasern deutlich abzuzeichnen.

Nachdem der Markteintritt mit den ersten Fasertypen vor allem in einzelnen hochpreisigen Segmenten gelang, werden nun mit der Marktausweitung deren spezifische Vor- und Nachteile in den einzelnen Stufen der textilen Weiterverarbeitung und der Endnutzung deutlich. Der derart immer besser definierte Entwicklungsbedarf und das zunehmende Wissen um die Möglichkeiten, das Eigenschaftsspektrum zu modifizieren, lassen das ursprüngliche Ziel einer neuen, im breitesten Umfang einsetzbaren „Baumwolle-plus“ in absehbarer Nähe rücken.

Aber auch bei der Entwicklung von Lyocell Fasern mit speziellen Funktionalitäten - teils

für völlig neue Anwendungen - und bei den Ansätzen einer Nutzung der Lyocell-Technologie für Produkte fernab der bisher im Zentrum der Entwicklungsanstrengungen stehenden Fasern, wird immer klarer, dass die direkte Regeneration der Cellulose aus organischer Lösung eine neue Dimension bei der Nutzung des hervorragenden Eigenschaftspotentials dieses wichtigsten „organischen Konstruktions- und Funktionswerkstoff“ der Natur ermöglicht.

Lyocell bietet nicht nur die Chance für eine neue Generation cellulosischer Fasern - auch für bisher nicht zugängliche Einsatzgebiete, sondern auch für eine allgemeine Renaissance der Cellulose für unterschiedliche Produkte, bei denen sie entweder in den letzten Jahrzehnten durch vollsynthetische Polymere substituiert wurde oder bei denen völlig neue Anwendungen für dieses hervorragenden, natürlichen Polymers erschlossen werden.

Lassen Sie mich aus gegebenem Anlass<sup>1</sup> über das Thema Lyocell hinausgehend das Potential und die Situation von Cellulosefasern etwas genereller behandeln und dabei mit einem kurzen Zitat aus der jüngsten Presseaussendung der Lenzing AG zum letzten Halbjahresergebnis beginnen. Da ist unter der Überschrift „Kapazitätsausbau zur Festigung der Weltmarktstellung“ folgendes zu lesen:

„Um die gestiegene Nachfrage der Kunden im Kerngeschäft Fasern optimal bedienen zu können und Wachstumschancen zu nützen, startete

die Lenzing-Gruppe im 1. Halbjahr ein umfassendes Investitionsprogramm. Bis Ende 2003 werden insgesamt EUR 125 Mio in die Kapazitätserweiterung an den Standorten Lenzing und Heiligenkreuz investiert. Die Faserproduktionskapazitäten in Lenzing werden um 20.000 Tonnen auf 200.000 Jahrestonnen angehoben. Parallel dazu wird zur Absicherung der Vollintegration die Zellstoffproduktion um 35.000 Tonnen auf 210.000 Jahrestonnen erhöht werden. Am Standort Heiligenkreuz wird eine zweite Produktionsstraße die Produktionskapazität auf 40.000 Tonnen jährlich verdoppeln. Mit der Inbetriebnahme der zusätzlichen Kapazitäten ist Ende 2003 zu rechnen.“

<sup>1</sup> Beitrag zum 5. Internationalen Symposium „Alternative Cellulose –Herstellen, Verformen, Eigenschaften“, Rudolstadt, 4.- 5. Sept. 2002.

Soweit die Lenzinger Neuigkeiten vom 29. August. Als ich den Titel dieses Vortrages plante, konnte ich die konkrete Aktualität noch nicht voraussehen. An vielen Reaktionen ließ sich allerdings ersehen, dass die Nachricht von der Fachwelt doch sehr mit Überraschung aufgenommen wurde. Der Zustand unserer Industrie lässt offenbar nur mehr Nachrichten von Betriebsschließungen erwarten und etliche Vertreter der Branche können nicht verstehen, wie man heutzutage noch neue Faserkapazitäten in Westeuropa installieren kann. Für Lenzing sind es bereits mehr als 100.000 Jahrestonnen, die in weniger als 10 Jahren in Betrieb gehen. Das ist wesentlich mehr als die kumulierten Schließungen anderer Produzenten in derselben Periode. Aber natürlich bleibt die Frage: ist Lenzing eine Ausnahme, oder wären wir besser beraten gewesen, dem Trend zu folgen?

Es sind ja tatsächlich in den letzten Jahren eine große Anzahl von Betrieben geschlossen worden und eine Reihe von traditionellen Faserproduzenten hat sich sogar vollständig aus dieser Industrie zurückgezogen. Die strategischen Marktanalysen ließen einen zunehmenden Druck auf die Erträge und ein langfristiges Schrumpfen des Verbrauches ihrer etablierten Produkte erwarten. Die Konsequenz war in den meisten Fällen eine reine „Melkstrategie“, die dann früher oder später zur Schließung während einer der nächsten Talphasen im Konjunkturzyklus führte. Vielfach ging man dabei auch von der Erwartung nach einer besseren Auslastung der noch verbleibenden Kapazitäten aus, was jedoch in der Regel nicht wirklich in Erfüllung ging, da der gesamte Markt aus der pessimistischen Grundstimmung heraus meist gleich mit verschwand. Auch Lenzing war von einem derartigen Fall betroffen, als wir uns der Entscheidung unseres Joint-Venture-Partners, die gemeinsame Polyesterstapelfaserfabrik in Lenzing zu schließen, nicht widersetzen konnten. Die Marktstruktur hat sich tatsächlich vollständig geändert und die deprimierte Stimmung bei vielen Vertretern der Industrie ist durchaus begreiflich. Es stimmt, dass große Teile der textilen Produktion in Niedriglohn-Länder abgewandert ist und dass die Textilindustrie noch immer unter dem Druck von Billigimporten stöhnt. Aber stimmt es wirklich, dass diese Entwicklung, die in den USA bereits zum fast schon vollständigen Verschwinden von Faserproduktion und Textil-

industrie geführt hat, auch in Europa unausweichlich ist?

Überraschenderweise hat nicht nur die Cellulosefaserproduktion in Europa wieder das Niveau der '80er Jahre erreicht, von denen es heißt, dass damals „die textile Welt noch in Ordnung war“. Auch bei Polyesterfasern hat - trotz der vielen Schließungen traditioneller Produzenten - eine Reihe neuer und kleinerer Spieler für sich Chancen identifiziert und sogar in neue Fabriken investiert (Abb. 1).

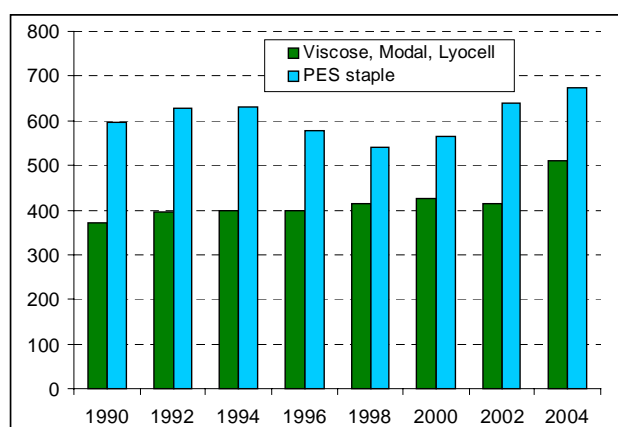


Abb. 1. Produktionskapazitäten in Westeuropa (tpa).

Offenbar erfassen die Marktanalysen der Schlüsselproduzenten nur einen Teil des Bildes. Es stimmt jedenfalls, dass der Markt weder bereit und wohl auch nicht fähig ist, weiterhin die von den Faserproduzenten erwarteten hohen Margen für Standardprodukte zu bezahlen; es stimmt aber auch, dass man darauf auch anders als nur mit Kapazitätsrücknahmen reagieren kann: die Zukunft der Industrie liegt wohl ein weiteres Mal darin, die Herausforderung anzunehmen und mit dem Erledigen der „Hausaufgaben“ zu beginnen: nämlich die Kostenbasis zu reduzieren, die Umweltprobleme zu lösen, die Qualität an die gestiegenen Anforderungen der Weiterverarbeiter anzupassen, neue Marktsegmente zu finden und die Kunden mit neuen innovativen Spezialfasern zu unterstützen. Aber natürlich passt diese Art von „Hausaufgaben“ nicht zu einer „Melkstrategie“. Die Lenzinger Großinvestitionen der letzten Jahre können andererseits nur vor diesem Hintergrund gesehen werden, und natürlich hat sehr viel davon mit Forschung und Entwicklung zu tun.

Lassen Sie mich deshalb einen weiteren kurzen Abschnitt aus der Lenzing Pressemitteilung zitieren: Hier heißt es unter „*Starke Nachfrage nach Spezialfasern*“:

*„Die positive Entwicklung des Fasergeschäftes der Lenzing Gruppe ist vor allem auf das breite Produktportfolio und die hohen Qualitätsstandards zurückzuführen: „Die Spezialisierung und der Ausbau der Kapazitäten tragen jetzt Früchte, ....*

*Der Absatz von Lyocell konnte gegenüber dem Vorjahr signifikant gesteigert werden. Die Anlage in Heiligenkreuz ist voll ausgelastet. Mit dieser Entwicklung wurden die Pläne übertroffen und das Ergebnis konnte deutlich verbessert werden.*

*Der Absatz der Spezialfaser Lenzing Modal lag um 43% über dem Vergleichswert des Vorjahres. Sehr erfreulich verlief auch die Entwicklung bei Nonwovens-Fasern.“*

Soweit die Pressemitteilung. Kontinuierliche Entwicklungsanstrengungen haben zu einer wesentlichen Verbesserung des Produktportfolios geführt, so dass - ausgehend von etwa 30 % vor 10 Jahren - Lenzing in der Zwischenzeit mehr als 60 % seiner Produktion in Spezialitätenmärkten absetzt.

Die Ausgangslage war natürlich hervorragend: Cellulose ist der wichtigste „organische Konstruktions- und Funktionswerkstoff“ der Natur und weist dementsprechend eine umfassende Palette hervorragender und sehr spezifischer Eigenschaften auf. Diese Eigenschaften können für verschiedenste Produkte zugänglich gemacht und auch gezielt modifiziert werden, sobald es einem gelingt, die Cellulose in Lösung zu bringen und sie dann in der gewünschten Form auf geeignete Weise zu regenerieren.

Die Verfahren entsprechen geradezu vorbildhaft der für unsere Zeit so wichtigen Vorgabe, mit nachwachsenden Werkstoffen nachhaltig zu wirtschaften. Der Verbrauch von Cellulosefasern steht im Einklang mit natürlichen Produktlebenszyklen und geht einher mit einer Entlastung der Umwelt. Holz ist ein nachwachsender Rohstoff und nahezu unbegrenzt verfügbar; die Produkte sind CO<sub>2</sub>-neutral (Treibhauseffekt / Kyoto) und sind biologisch abbaubar (Deponieproblematik).

Die Produkte entsprechen nach dem Ökotex Standard 100 der besten Klasse I. Die Ökobilanz ist im Vergleich zu allen Konkurrenzprodukten sehr günstig. Wälder nutzen Grenzertragsflächen

(Qualität, Klima, ....), sie brauchen keine künstliche Bewässerung, keinen Kunstdünger und auch keine Pestizide. Lenzing hat die Umweltthematik mit viel Einsatz aufgegriffen, so dass sie als vorbildlich gelöst gelten kann: gerade für integrierte Fabriken gilt, dass die Herstellung in nahezu völlig geschlossenen Stoffkreisläufen und energetisch nahezu autark erfolgen kann. Lenzing ist weltweit das führende Unternehmen in der „natürlichen“ Welt dieser Technologien.

Nicht umsonst hat die neue Lenzing-Lyocell unter allen europäischen Einreichungen den EU-Umweltpreis 2000 in der Kategorie „The Technology Award for Sustainable Development“ gewonnen (Abb.2)!



Abb. 2. EU-Umweltpreis 2000 für Lenzing Lyocell.

Die Möglichkeit die Eigenschaften des Rohstoffs in der eigenen Zellstoffproduktion zu steuern, die breite technologische Basis mit dem Viscose-, Modal- und Lyocell-Verfahren ermöglicht ein stetig wachsendes Angebot einer Vielzahl von Fasern für ganz spezielle Marktbedürfnisse.

Für diese hohe Innovationsleistung ist naturgemäß spezifische, hohe Kompetenz auf den Gebieten der Holz-, Cellulose- und Fasertechnologien nötig. Rund 130 hochqualifizierte Mitarbeiter bedienen sich dabei eines umfassenden Instrumentariums von Technikumsanlagen und analytischen Methoden:

- für Holzaufschluss und -bleiche,
- für Lösungsherstellung nach dem Viscose-, Lyocell- und Acetatverfahren,
- für die Herstellung von Viscose-, Modal- und Lyocellfasern und
- für Lyocell Folien und andere alternative, auf dem Lyocell-Prozess basierende Produkte.

Diese Kompetenz wird ergänzt durch kooperative Projekte, durch langfristig etablierte kooperative Forschungseinrichtungen gemeinsam mit Universitäten und anderen Unternehmen und durch einen breit gestreuten Forschungsdiestleistungsverkauf, der es auch ermöglicht, das spezialisierte, teure Forschungsinstrumentarium besser auszulasten und überkritisch zu bleiben. Als Träger der Innovationsbemühungen konnte sich die Lenzing auf diese Weise in den letzten Jahren ein einzigartiges Kompetenznetzwerk auf ihrem Gebiet aufbauen (Abb.3).



Abb. 3. Kompetenznetzwerk Cellulose- und Fasertechnologie.

Obwohl die klassischen manmade Cellulosefasern bereits über 100 Jahre alt sind, so wird doch noch immer mit Erfolg intensiv an verbesserten Eigenschaften und an neuen Fasertypen für spezielle Anwendungen gearbeitet. Darüber hinaus ist es Lenzing gerade in den letzten Jahren mit der neuen Lyocell-Technologie gelungen, eine neue Fasergeneration zu entwickeln und damit einen großen Schritt auf dem Weg zu einem noch breiteren und vielseitigeren Einsatz von manmade cellulose weiterzukommen.

Die Intensität des laufenden Innovationsprozesses lässt sich anschaulich aus der Anzahl der seit 1997 von Lenzing herausgebrachten neuen Spezialitäten ablesen: Auf Basis des Viscose- und Modalverfahrens sind dies Viscostar, Viscofresh, Modal Sun, Modal Fresh und eine Modal Color Faser; auf Basis des neuen Lyocellverfahrens sind es ProModal, ProViscose, Lyocell, Lyocell Tech und Lyocell NW (Abb.4).

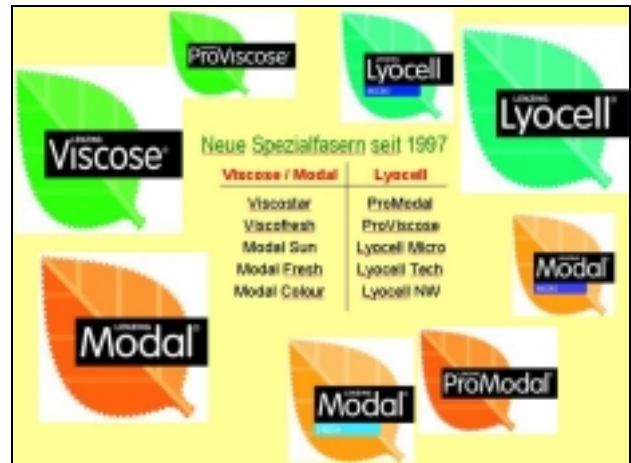


Abb. 4. Neue Lenzinger Spezialfasern seit 1997.

Alle Lenzinger Faserentwicklungen drehen sich naturgemäß immer auch um die einzigartigen, vor allem auch physiologisch hervorragenden Eigenschaften, die die Cellulose mitbringt. Nicht umsonst werden die Lenzinger Fasern durch Attribute wie *„Makes the world a softer place“* (Lyocell) oder *„The feel good fibre“* (Modal) beworben. Es ist leicht einsichtig, dass gerade in Ländern mit hohen Durchschnittstemperaturen und hoher Luftfeuchtigkeit das gute Klima- und Feuchtigkeitsmanagement von Cellulose unverzichtbar für die tägliche Bekleidung ist. Doch gilt derartiges nicht nur für den Bekleidungssektor, sondern auch für die unterschiedlichsten nonwovens-Anwendungen! Mit steigender Weltbevölkerung und einem mit dem Wohlstand steigenden spezifischen Faserverbrauch wird auch der Bedarf an Cellulosics weiter zunehmen (Abb.5). Eines der wesentlichsten Entwicklungsvorhaben der Lenzing ist dementsprechend eine „Baumwolle plus“, mit allen Vorteilen der bisherigen manmade-Cellulosics, aber ohne deren bisherige Schwächen. Dies geschieht auf Basis der Lyocell-Technologie, da Viscose aufgrund eines von Baumwolle zu verschiedenen Eigenschaftsprofils hierzu nicht in der Lage ist. Lyocell stellt bereits heute einen großen Fortschritt in Richtung

baumwollähnlicher Eigenschaften dar (Abb.6) und findet schon Anwendungen in Bereichen, in

denen bisher ausschließlich hochwertigste Baumwolltypen zum Einsatz gelangten.

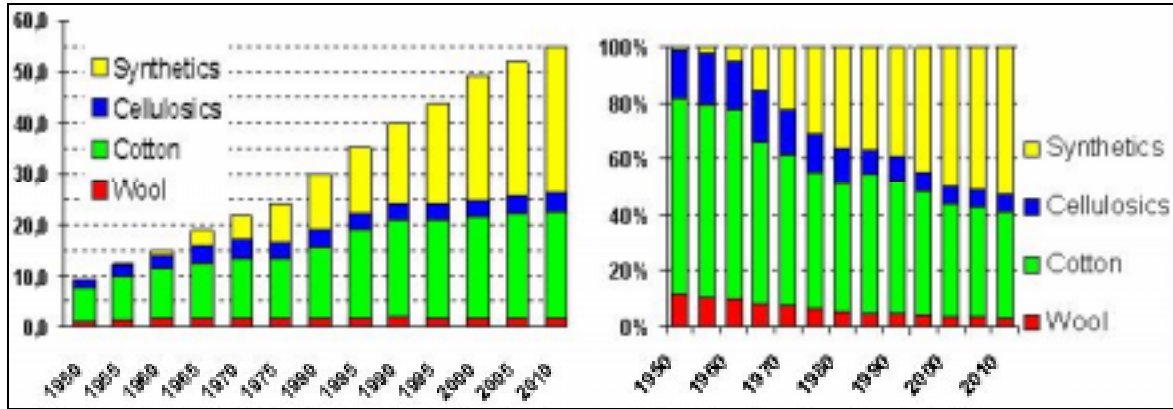


Abb. 5. Entwicklung des Weltfaserverbrauchs (Mio t) 1950 bis 2010.

Eigenschaften konditioniert:	Viscose		Modal		Lyocell		Baumwolle	
	von	bis	von	bis	von	bis	von	bis
Festigkeit	24	26	34	36	40	42	24	26
Dehnung	18	20	12	14	15	17	7	9
Schlingenfestigkeit	7	8	8	8	16	20	20	20
Feuchtigkeitsaufnahme	14		13		12		7	
Eigenschaften maß:								
Festigkeit	10	13	20	22	34	36	40	
rel. Naßfestigkeit	50		55	60	85		100	
Dehnung	21	23	13	15	17	19	9	11
BISFA Naßmodul	2,0	3,0	5,5	6,5	9,0	10,0	8,0	12,0

Abb. 6. Faserdaten ausgewählter Cellulosics.

Die Kraft-Dehnungskurven von Lyocell und Baumwolle haben im Bereich niedriger Dehnungen fast identen Verlauf. Das Arbeitsvermögen von Lyocell ist sogar um vieles höher, die Nass-eigenschaften sind die besten unter allen man-made-Cellulosics, und auch Sprödigkeit bzw. Schlingenfestigkeit sind hervorragend.

Elastizitätsmoduli lässt zwar insgesamt höhere Werte bei Cellulose I erwarten, indiziert aber noch immer ein theoretisches Verbesserungspotential um eine ganze Größenordnung bei Cellulose II (Abb.7).

Fasern		E [GPa]	
		Praktisch	Berechnet(*)
Hanf	(Cellulose I)	29	136
Baumwolle	(Cellulose I)	6 – 11	136
HT-Rayon	(Cellulose II)	13	89
Viskose	(Cellulose II)	4 – 9	89

Abb. 7. Elastizitätsmoduli ausgewählter Cellulosics (\*) Cellobiose-Molekül als Grundeinheit [MM2HB molecular mechanics program].

Insgesamt ist das theoretische Potential der polymeren Werkstoffe mit Bezug auf mechanische Eigenschaften auch bei Cellulose noch bei weitem nicht genutzt: die Differenz zwischen gemessenen und quantenmechanisch berechneten

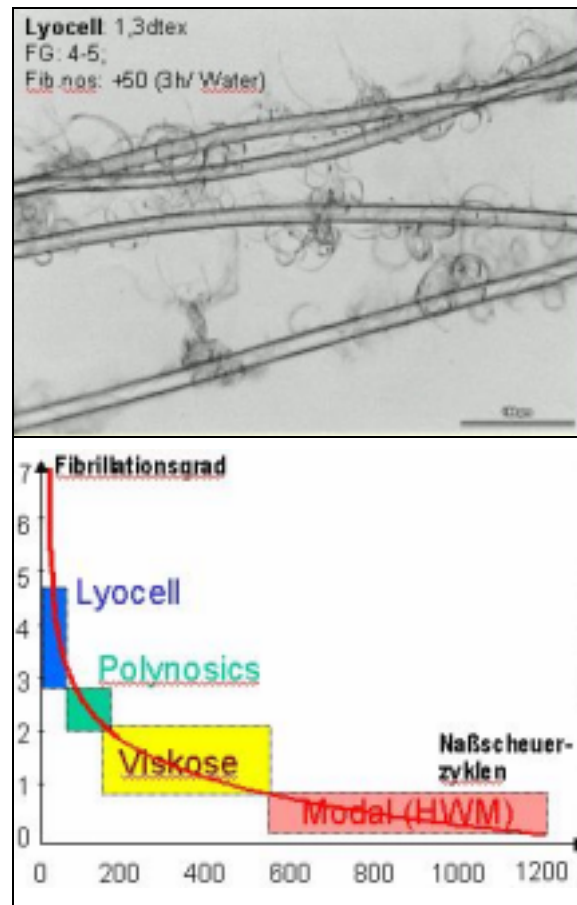


Abb. 8. Fibrillationsverhalten von Cellulosics.

Hauptthema der Entwicklungsanstrengungen bei Lyocell bleibt derzeit jedoch die Suche nach Wegen für die Steuerung des relativ hohen Fibrillationsniveaus (Abb. 8), das derzeit für unvernetzte Lyocellfasern noch einen gewissen Aufwand für zusätzliche Veredelungsschritte erforderlich macht, wenn man sie für manche textile Applikationen einsetzen will.

Im Rahmen einer Einstiegsmarketing-Strategie und bis zum Erreichen des genannten Zieles einer allgemein und einfach einsetzbaren Massentextilfaser ist die Produktentwicklung bei Lyocell durch eine möglichst zielgerichtete Nutzung spezifischer Eigenschaften für einzelne high-end Nischen geprägt. Es handelt sich hierbei einerseits um den Lenzinger Schwerpunkt *Nonwovens Anwendungen* aber auch um *Heimtextilien* mit einem Einsatz bei Bett-, Frottier- und Dekotextilien. Bei ihnen spielt der natürliche Ursprung, die Reinheit, der Komfort und die Ästhetik neben der grundlegenden textilen Performance eine besondere Rolle. Teilweise sind es höchst überraschende Aspekte, die interessante neue Produkte ermöglichen. So ähnelt z.B. die Faseroberfläche von Lyocell, im Gegensatz zu den Viscosetypen eher der von Synthetics (Abb.9).

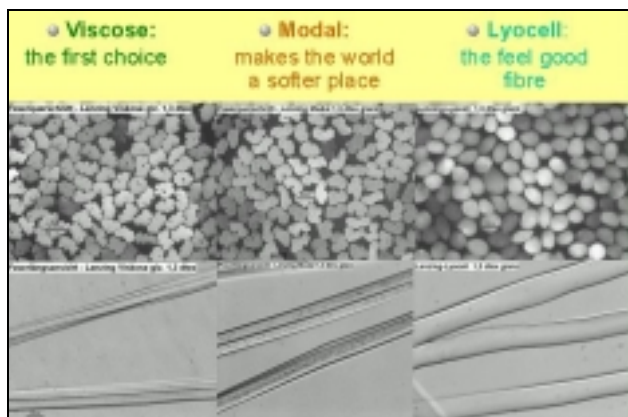


Abb. 9. Quer- und Längssicht von Viscose, Modal und Lyocell.

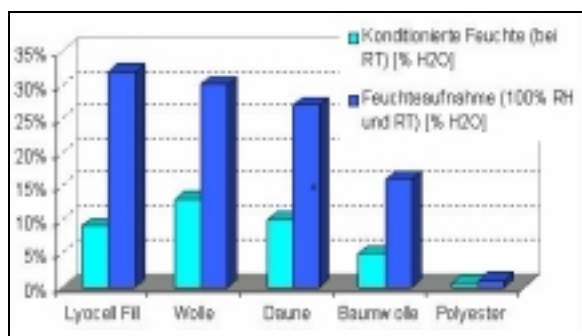


Abb. 10. Feuchtigkeitsaufnahme von Füllfasern.

Dies bewirkt im Verbund mit dem sehr anderen Mikro-Aufbau der Cellulosematrix bei Lyocell nicht nur eine andere Optik und Haptik, sondern auch deutliche Unterschiede mit Bezug auf den Strömungswiderstand, die thermische Isolation und die Wasserdampfsorption. Lyocell kann erstaunlich große Feuchtigkeitsmengen reversibel speichern (Abb.10).

Aus derartigen Unterschieden wiederum lässt sich vielleicht verstehen, warum Lyocell im Vergleich zu anderen Fasern ein gänzlich anderes Mikroklima in den Hautkontaktzonen und damit wiederum signifikant unterschiedliche tragephysiologische Eigenschaften hat.

Ein weiteres Gebiet, auf dem spezifische, inhärente Eigenschaften von Lyocell den Weg für überraschend neue Anwendungen öffnen, ist deren vergleichsweise hohe Reinheit. Neben den vielfach diskutierten Resten von Pestiziden enthält Baumwolle ganz natürlich auch vergleichsweise sehr hohe Anteile von Schwermetallen (Abb.11). Viscose enthält als Verunreinigungen vor allem aus dem Herstellprozess stammendes Natrium und Restschwefel.

	Cotton	Lyocell
Fe	39,4	3 bis 5
Zn	20,2	1 bis 3
Cr		< 0,6
Ni		< 0,4
Pb		< 0,2
Cu		< 0,2
Cd		< 0,01

Abb. 11. Schwermetallgehalt von Baumwolle und Lyocell (mg/kg).

	Lenzing Lyocell	Tencel	Lenzing Viscose normalgebleicht	Lenzing Viscose chlorfrei-gebleicht
3 min 134 °C	0	-1	-2	-5
10 min 126 °C	0	-1	-2	-6
15 min 121 °C	0	-2	-2	-6
4 min 138 °C	-1	-2	-3	-7
15 min 138 °C	-2	-3	-7	-11
30 min 138 °C	-5	-4	-11	-15

Abb. 12. Vergilbung: Abfall des Tappi-Weißgrades nach Wärmebehandlung (Sterilisation).

Da reine Cellulose aber auch nahezu rückstandsfrei pyrolysiert, kann diese Reinheit z.B. für die Herstellung keramischer Katalysatoren mit genau



steuerbarer Porenstruktur verwendet werden. Die hohe Reinheit ist auch eine der Ursachen dafür, dass Lyocell bedeutend unempfindlicher gegen intensive Wärmebehandlung ist, dass sie z.B. bei der Sterilisation deutlich weniger vergilbt als andere Cellulosics (Abb.12).

Über die Anwendung in Fasern hinaus scheint sich aber mehr und mehr zu bestätigen, dass sich die teuer entwickelte NMMO Lösungs- und Rückgewinnungstechnologie auch für alternative Produkte nutzen lässt (Abb. 13). In Kooperation mit Firmen, die marktseitig andere Interessen haben, ist Lenzing deshalb intensiv mit der Entwicklung neuer Produkte auf Basis dieser Technologie beschäftigt.

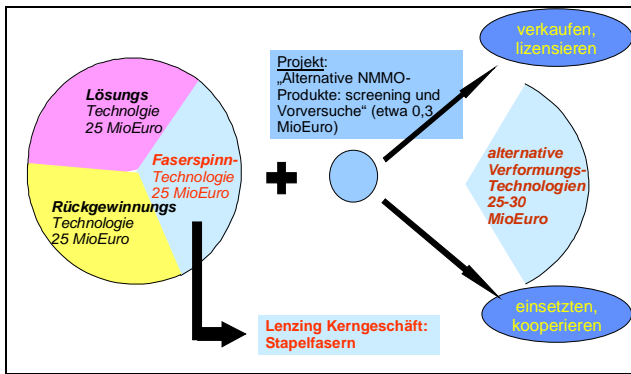


Abb. 13: Alternative Produkte durch Lyocell-Technologie.

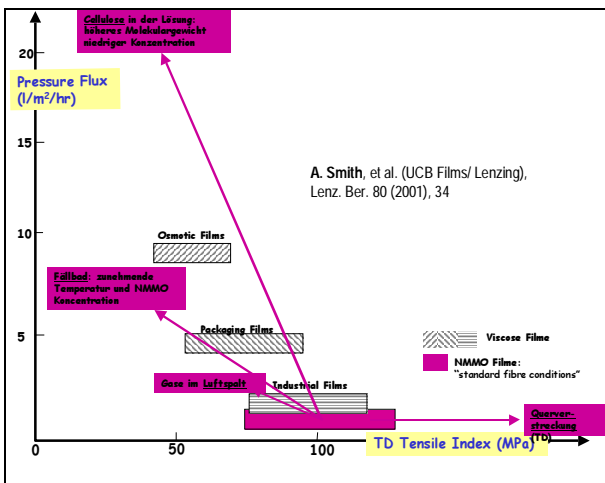


Abb. 14. Permeabilität von Lyocellfolien.

So wird derzeit z.B. an der Herstellung neuer Schwammstrukturen aus Celluloselösungen in NMMO gearbeitet. Weiters konnten Folien entwickelt werden, deren Eigenschaften durch die Wahl geeigneter Prozessparameter in weiten Bereichen beeinflussbar sind. Die guten mechanischen Eigenschaften, die erreichbaren Flussraten

und die Fähigkeit der Cellulose, Moleküle zu trennen, machen derartige Folien für eine Reihe neuer und hochwertiger Membranapplikationen wesentlich besser nutzbar, als dies mit Cellophan der Fall ist. Derartige „Lyocell-Folien“ können z.B. auch als osmotische Membranen in Wasserreinigungscontainern zum Einsatz gelangen (Abb.14, 15).

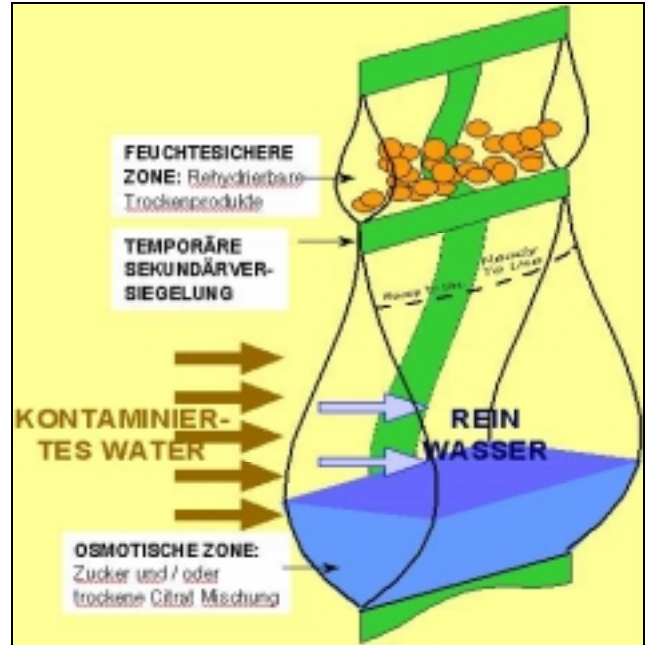


Abb. 15. Osmotischer Wasserreinigungs-Container.

Die offeneren Cellulosestrukturen ermöglichen einerseits einen wesentlich verbesserten Wassertransport durch die Membran hindurch, während andererseits eine feine Innenbeschichtung der Membran die Dialyse der vorgelegten Substanzen (z.B. Zucker) aus der Osmosezone heraus verhindert. Der osmotische Druck und die Hydrationsrate bleiben hierdurch ausreichend lange aufrecht.

Bei all diesen „neuen Anwendungen“ des Lyocell-Verfahrens wird deutlich, dass die direkte Regeneration der Cellulose aus organischer Lösung eine völlig neue Nutzung ihres hervorragenden Eigenschaftspotentials ermöglicht. Lyocell öffnet also nicht nur die Chance für eine neue Generation cellulosischer Fasern - auch für ganz neue Einsatzgebiete - sondern auch die einer Renaissance der Cellulose in verschiedensten Werkstoffen, die einerseits, wegen der Notwendigkeit zu derivatisieren, in den letzten Jahrzehnten dem zunehmenden Substitutionsdruck vollsynthetischer Polymerer weichen mussten und die andererseits völlig neue Produkte ermöglichen werden.

Zusammenfassend lässt sich feststellen, dass es sehr wohl möglich ist, in Europa mit Fasern erfolgreich zu sein, wenn man die Herausforderungen annimmt und sich neu auf die traditionellen Tugenden der typisch europäischen produzierenden Industrie besinnt. Die jüngsten Vorkommnisse in einer Reihe von „Mega-Dienstleistern“ und sogenannten „neuen“ Industrien in den Vereinigten Staaten haben klar gemacht, dass kontinuierliche Steigerungsraten und ununterbrochen zweistellige Profitabilitäten entgegen dem zeitweiligen Anschein doch nicht realistisch sind. Wir haben gute Chancen, wenn wir uns auf Effizienz, Flexibilität und Diversifikation konzentrieren. All das erfordert aber eine Kultur von

Stabilität und Langfrist-Denken. So wie Produktionsanlagen nicht ohne langfristig wirksame Instandhaltung und Ersatzinvestitionen funktionieren können, so kommt es ohne konsistente und kontinuierliche Forschungsanstrengungen und gut ausgebildete und motivierter Mitarbeiter auch zu keinen innovativen Produkten und neuen Technologien. Auch hierfür bedarf es eines speziell sorgsamem Umgangs und gezielter Maßnahmen im Sinne eines langfristigen Kompetenzaufbaus, wobei sich die Zeichen mehren, dass man auch der Verfügbarkeit des Nachwuchses wesentlich mehr Augenmerk widmen muss als bisher.

## **LYOCELLMISCHUNGEN - DER ZUSATZNUTZEN FÜR DIE TEXTILINDUSTRIE**

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**Lyocell-Fasern unterscheiden sich von den herkömmlichen, bisher am Markt bekannten Zellulosefasern durch ihr umweltfreundliches Herstellungsverfahren und ihre hervorragenden Fasereigenschaften, wie Festigkeit im trockenen und nassen Zustand, und durch die ausgezeichnete Dimensionsstabilität der daraus hergestellten Flächengebilde. Außerdem zeichnen sich Flächengebilde aus Lyocell aufgrund ihrer speziellen Fasereigenschaften in ihrer Ästhetik, wie Optik und Brillanz, zusätzlich durch einen kühlen, trockenen Griff aus.**

**Lyocell-Fasern unterscheiden sich wesentlich von klassischen Zellulosefasern, vor allem durch ihre hohe Fibrillationsneigung. Die Fibrillation ermöglicht einerseits die Herstellung bzw. Produktion von verschiedenen modischen Griff/Optik-Effekten, andererseits können durch die Fibrillation sowohl in der Verarbeitung/Veredelung als auch im Fertigprodukt Probleme auftreten. Durch geschickte Mischungskombinationen und**

**Konstruktionen in der Fläche können die positiven Eigenschaften dieser Faser- generation - gepaart mit den Fasereigenschaften des Mischungspartners, z.B. Modalfasern - zu hervorragenden Produkten führen, die sowohl modisch als auch kommerziell äußerst interessant sind. Die Verwendung von Rotorgarnen ermöglicht eine besonders wirtschaftliche Herstellung von Endprodukten, die hohe Qualitätsanforderungen erfüllen, wie dies bisher noch nicht möglich war.**

**Für die im Vortrag vorgestellten Lyocell-Artikel sind keine speziellen Veredelungsschritte, wie sie bisher für diese Faser- generation notwendig waren, erforderlich, d.h., für die Ausrüstung dieser Artikel wurde ein normaler Maschinenpark, wie er für die bekannten Zellulose regeneratfasern verwendet wird, eingesetzt. Die Kombination von Produktivität, User-Economics, gepaart mit einer hohen Fertigprodukt-Qualität zeigt interessante Vorteile für den Endverbraucher.**

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### **Lyocell-Mischungen - der Zusatznutzen für die Textilindustrie**

Lyocell-Fasern unterscheiden sich von den herkömmlichen - bisher am Markt eingeführten - Cellulosefasern durch ihr umweltfreundliches Herstellungsverfahren und ihre hervorragenden Fasereigenschaften, wie z. B. der Festigkeit im trockenen und nassen Zustand, und durch die ausgezeichnete Dimensionsstabilität der daraus hergestellten Flächengebilde.

Die Lenzing AG ist weltweit führend auf dem Gebiet der Cellulosefasern. Das Portfolio umfasst nicht nur reguläre Viscosefasern, ein besonderer Schwerpunkt wird in Lenzing auf

die Produktion von Spezialfasern gelegt. Neben den am Markt sehr erfolgreich etablierten Produkten, wie Modal, schwer-entflammbare Viscosefasern, Spezialfasern für Nonwovens und Spinnfarben, produzieren wir seit 1997 auch Lyocellfasern. Lyocellfasern stellen die neueste Generation von Cellulosefasern dar und unterscheiden sich wesentlich durch die Fibrillierneigung. Die Fibrillation ermöglicht einerseits die Herstellung bzw. Produktion von verschiedenen modischen Griffoptiken, andererseits können dadurch - sowohl im Fertigprodukt wie auch in der Verarbeitung - Probleme auftreten (z. B. ein höherer Anfall an 2. Qualität).

Durch geschickte Mischungskombinationen und Konstruktionen in der Fläche können die positiven Eigenschaften von Lyocellfasern - gepaart mit den Eigenschaften der Mischungspartner, wie Baumwolle, Modal oder Viscose - zu hervorragenden Produkten führen, die sowohl modisch als auch kommerziell äußerst interessant sind.

Die textilen Eigenschaften von Lyocell sind mit jenen von hochwertigster, langstapeliger Baumwolle zu vergleichen, bzw. sind dieser, wie später noch demonstriert, sogar überlegen. In der Nassfestigkeit eröffnen sich für cellulosische Fasern bisher ungeahnte Möglichkeiten.

Während Baumwolle mit einem weltweiten Angebot von ca. 19.000.000 t – davon langstapelige Baumwolle mit 600.000 t – in der Textilindustrie gut eingeführt ist, steht die Markteinführung von Lyocell am Beginn.

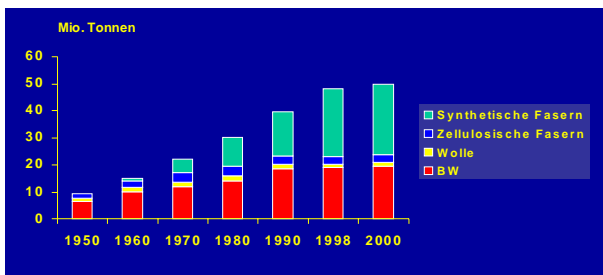


Abb. 1a. Weltfaserverbrauch.

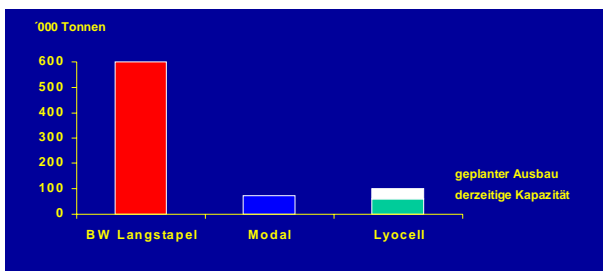


Abb. 1b. Weltproduktion bzw. -kapazität.

Die derzeit installierte Kapazität von Lyocell liegt bei ca. 100.000 t. Schon daraus ist ersichtlich, dass dieser Fasergeneration künftig ein besonderer Stellenwert gegeben wird und somit eine universelle Anwendung angestrebt werden muss.

Die Lenzing AG sowie auch unsere Mitbewerber sind von der Zukunft von Lyocellfasern überzeugt und setzen verstärkt entwicklungs-technische Maßnahmen, um die

Markteinführung dieser Fasergeneration zu beschleunigen.

Lyocellfasern wurden bisher hauptsächlich in hochpreisiger Designerbekleidung eingesetzt. Die Verwendung von Lyocell bei der Herstellung von Textilien verlangt jedoch spezielle Verfahrensschritte, die kostenintensiv und arbeitsaufwendig sind, z. B. enzymatische Ausrüstung. Dieser Umstand hat bisher den Einsatz von Lyocell limitiert.

Unsere Marketingpolitik geht nun dahin, mit der Entwicklung neuer Fasertypen und Textilkonstruktionen breitere Anwendungsgebiete zu erschließen, die die vorhin aufgezeigten Hindernisse beseitigen.

Bessere User-Economics sind für die Anwender von großer Bedeutung und können mit Produkten aus Lyocell bzw. Lyocell-Mischungskombinationen in folgenden Einsatzbereichen gut umgesetzt werden.

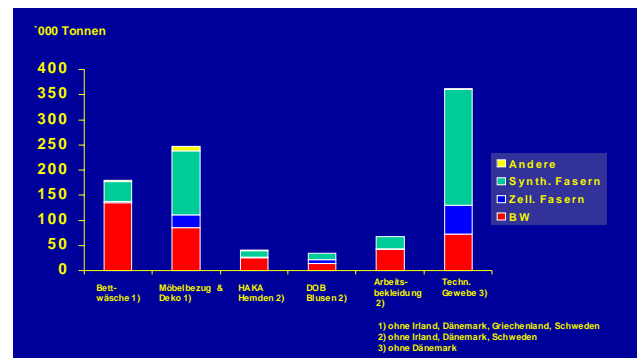


Abb. 2. EU Fasereinsatz.

Der in diesen Einsatzgebieten hohe Anteil von Baumwolle kann mit Lyocell bzw. Lyocell-Mischungskombinationen zur Erreichung besonderer Eigenschaften gut ergänzt werden. Speziell in hochindustrialisierten Ländern, wo einerseits qualitativ hochwertige Produkte gefragt sind und andererseits Lohn- bzw. Herstellerkosten eine große Rolle spielen, können Lyocellmischungen als innovative und wirtschaftliche Alternative zu Baumwolle gesehen werden.

In den folgenden Ausführungen möchte ich einige Möglichkeiten darstellen, wie Lyocell in Kombination mit Mischungspartnern sinnvoll im Hinblick auf Produktqualität und Wirtschaftlichkeit eingesetzt werden kann. Hier spielt die hohe Faserfestigkeit von Lyocell eine dominante Rolle, die in den verschiedensten Mischungen Produkte ermöglicht, die bisher nicht

am Markt waren. Bei geeigneter Materialkombination ist es auch möglich die besondere Eigenschaft des Fibrillierens von Lyocell zu umgehen, ohne spezielle Ausrüstungsverfahren verwenden zu müssen. Die besonderen Produkteigenschaften der Lyocell-Faser wie

- Hohe Festigkeit
- Excellente Maßstabilität
- Besonderer Griff
- Besondere Optik

müssen ideal kombiniert und ausgenutzt werden. Setzt man in geeigneten Konstruktionen Lyocell oder Lyocellmischungen ideal ein, kann man hervorragende, wirtschaftlich hochinteressante Produkte herstellen.

In naher Zukunft wird eine nicht-fibrillierende Lyocellfaser unser Faserangebot ergänzen, womit völlig neue Produktperspektiven eröffnet werden. Die Entwicklung wird in Kürze abgeschlossen sein und in kommerzielle Produktion übergeführt.

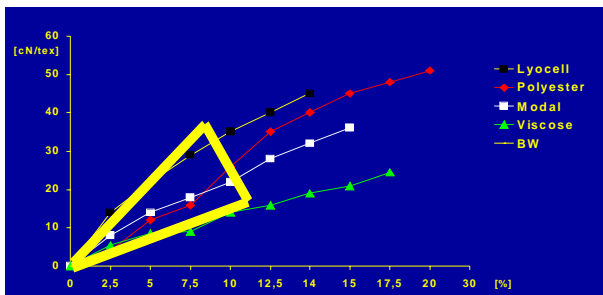


Abb. 3b. Kraft-Dehnungsverhalten.

Die neue, nicht fibrillierende Lyocell-Faser ist so konstruiert, dass man das Fibrillieren der Textilien vom absoluten Nicht-Fibrillieren bis zu einem gewünschten Fibrillieren steuern kann. Mit dieser Faser eröffnen sich völlig neue Perspektiven, wobei die idealen End-einsatzbereiche, wo die Stärken dieser Faser voll zum Tragen kommen, erst herausgearbeitet werden müssen.

Ich möchte heute einige Beispiele demonstrieren, wo Lyocellfasern in Intim- oder Systemmischung mit Viscose, Modal oder Baumwolle verarbeitet worden sind, wobei Textilien mit besonderen Eigenschaften hergestellt werden konnten. Es kommen Lyocellfasern mit normalen Fibrillier-Eigenschaften zum Einsatz. Die Verwendung von Rotorgarnen ermöglicht eine besonders

wirtschaftliche Herstellung von Endprodukten, die hohe Qualitätsanforderungen erfüllen, wie dies bisher noch nicht möglich war. In der Rotortechnologie, wo die Garnfestigkeit aufgrund der Fasereinbindung grundsätzlich schlechter ist als die von Ringgarnen, kommt die Faserfestigkeit von Lyocell speziell zum Tragen.

Untersuchungsreihen, die vor nicht allzu langer Zeit mit dem Textilinstitut Denkdorf durchgeführt wurden, zeigten, dass bis zur Markteinführung von Lyocell keine cellulosische Faser in der Lage war, die notwendigen Garnfestigkeiten von ca. 16 cN/tex, die für die Kettauglichkeit in der Weberei notwendig sind, zu erreichen.

Mit Lyocell sind wir nunmehr in der Lage, Garnfestigkeiten zu erzielen, die unter ausgezeichneten Verarbeitungseigenschaften an der Rotorspinmaschine hergestellt werden können und die zudem an der Webmaschine hervorragende Laufeigenschaften garantieren. Ein weiterer Vorteil dieser hochfesten Faser ist, dass wir heute schon sagen können, dass wahrscheinlich in naher Zukunft der Schlichteprozess für Lyocell-Rotorketten mit nicht allzu dichter Belegung entfallen kann bzw. ein Kaltschlichten völlig ausreichend ist.

Untersuchungen, die wir in diese Richtung angestellt haben, stimmen uns äußerst optimistisch. Selbstverständlich wird es hier notwendig sein, spezielle Spinnmittel zur Anwendung zu bringen, da auch die Haarigkeit einen entscheidenden Einfluss hat, und nicht nur die Faserfestigkeit von Bedeutung ist. Wie Beiträgen der Fa. Schlafhorst entnehmbar, wurden bereits Entwicklungen mit Lyocell und Lyocell-Mischungen, die in diese Richtung gehen, durchgeführt, und diese sind sehr vielversprechend ausgefallen.

Für alle Lyocell-Mischartikel, die wir bisher entwickelt haben, sind keine speziellen Veredelungsschritte, wie sie bisher für diese Fasergeneration erforderlich waren, notwendig. D.h., für die Ausrüstung dieser Artikel wurde ein normaler Maschinenpark, wie er für die heute am Markt befindlichen bekannten Cellulose-Regeneratfasern verwendet wird, eingesetzt.

## Modal / Lyocell-Mischungen

Im Rahmen interner Vergleiche wurden die charakteristischen Eigenschaften von 100 % Lyocell, 100 % Modal und einer Mischung Modal/Lyocell untersucht. Das Mischungsverhältnis wurde mit 70 % Modal und 30 % Lyocell gewählt.

Alle Gewebe wurden aus Ringgarn der Feinheit Nm 50/1 in identer Konstruktion bei gleichen Verarbeitungsbedingungen in unserer Weberei hergestellt. Sämtliche Gewebe wurden gesengt, breit vorbehandelt und im Jet reaktiv gefärbt. Alle Varianten wurden hochveredelt, wobei praxisübliche Kunstharzmengen (50 g/l) gewählt wurden. Die Ergebnisse lassen sich wie folgt interpretieren:

### Gewebefestigkeit

Auf Grund der hohen Garnfestigkeiten von Lyocellgarnen, liegt die Festigkeit des Gewebes aus 100 % Lyocell mit 80 daN deutlich über den Festigkeiten von Geweben aus Modal. Aus der Praxis wissen wir, dass Mischungen die Eigenschaften textiler Flächen optimieren.

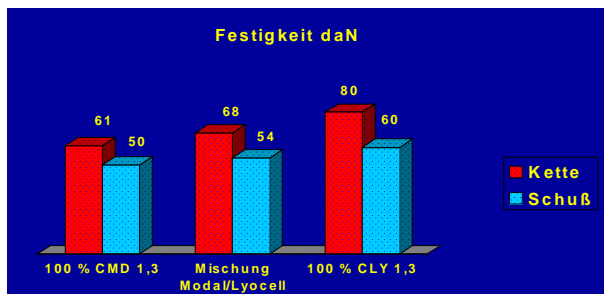


Abb. 4. Modal/Lyocell-Mischungen: Gewebevergleich – Ringgarn Nm 50/1: Festigkeit.

Die Modal/Lyocell-Mischung führt zu einer Steigerung der Gewebefestigkeit um etwa 10 % im Vergleich zum Gewebe aus 100 % Modal. Dieses Ergebnis war auf Grund der erhöhten Garnfestigkeit der Mischung Modal/Lyocell auch zu erwarten.

### Gewebedehnung

Die Modal/Lyocell-Mischung führt zu keiner Änderung der Gewebedehnung im Vergleich zu Artikeln aus 100 % Modal, ist aber signifikant günstiger als Artikel aus 100 % Lyocell.

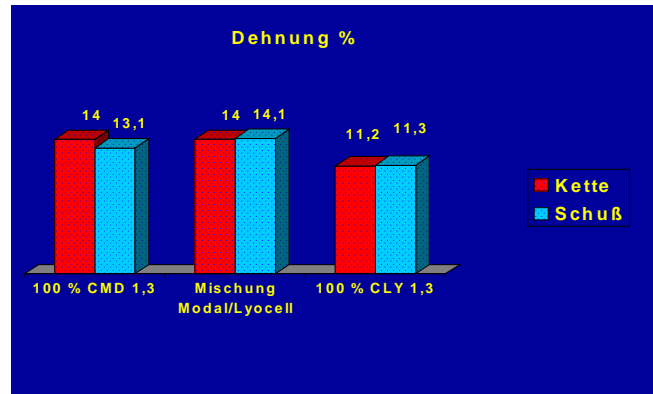


Abb. 5. Modal/Lyocell-Mischungen: Gewebevergleich – Ringgarn Nm 50/1: Dehnung.

### Pilling

Die Pillingprüfung nach Martindale der geprüften Artikel zeigt ein interessantes Ergebnis. Über den gesamten Verlauf des Pillingtests zeigt das Gewebe aus 100 % Lyocell ein gleichmäßiges Pillverhalten.

Mit der Pillnote 4,5 (Bestwert 5,0) liegt das Ergebnis der Pillingprüfung auf einem sehr hohen Niveau. Mit der Pillnote 4,5 zeigt die Modal/Lyocell-Mischung ein gleich gutes Ergebnis wie 100 % Lyocell und ist signifikant günstiger als das Gewebe aus 100 % Modal.

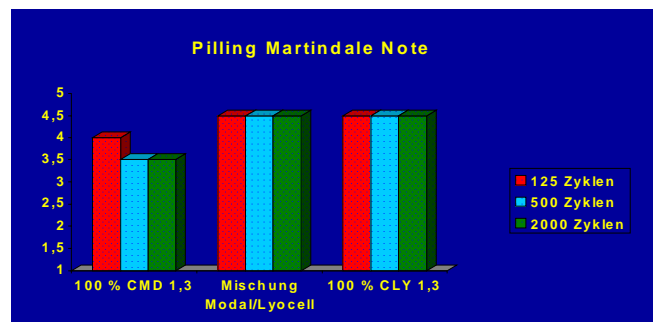


Abb. 6. Modal/Lyocell-Mischungen: Gewebevergleich – Ringgarn Nm 50/1: Pilling.

### Dimensionsstabilität

Es ist darauf hinzuweisen, dass die Maßänderung von 100 % Viscose und 100 % Modal grundsätzlich etwas höher liegt als Baumwolle bzw. Lyocell. Durch die Beimischung von Lyocell konnte die Dimensionsstabilität des Mischgewebes gegenüber von 100 % Modal deutlich verbessert werden.

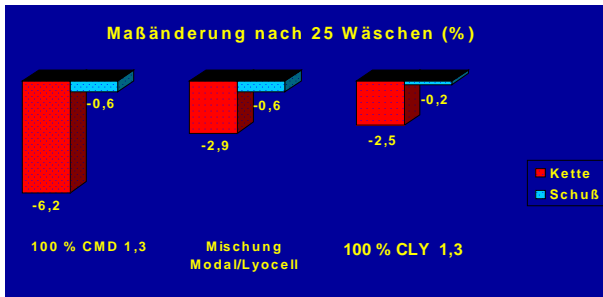


Abb. 7. Modal/Lyocell-Mischungen: Gewebevergleich – Ringgarn Nm 50/1: Massänderung.

## Lyocell / Baumwoll - Mischungen

In einem Gewebevergleich K 2/1 wurden verschiedene Kettgarne miteinander verglichen. Zum Einsatz kamen 100 % Lyocell Rotorgarn, 100 % Modal Ringgarn, 50/50 % Modal/Baumwolle Ringgarn und 100 % Baumwoll Ringgarn. Als Schuss wurde 50/50 % Modal/Baumwoll Ringgarn verwendet.

Wie dieser Gewebevergleich zeigt, können die positiven Faser- und Garneigenschaften von Lyocell trotz Verwendung von Rotorgarnen hervorragend ins Fertiggewebe übertragen werden.

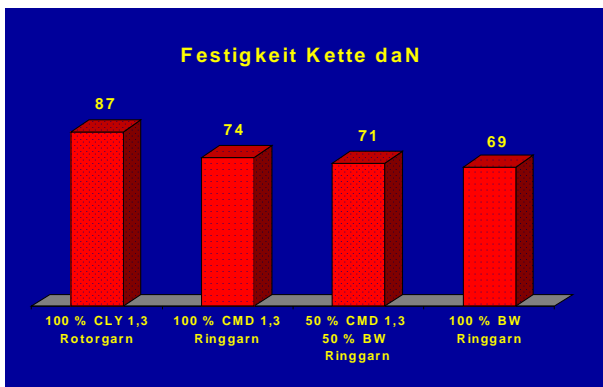


Abb. 8. Lyocell-Baumwolle-Systemmischungen: Gewebevergleich – Körper 2/1, Nm 50/1: Festigkeit.

Neben den günstigen Festigkeiten hat Lyocell auch einen sehr positiven Einfluss auf die Pillingresistenz. Die Pillingprüfung erbrachte für diese Gewebekonstruktion eindeutig die besten Werte. Es ist klar erkennbar, dass ein

Lyocell-Rotorgarn einem 100 % Baumwoll-Ringgarn - in der richtigen Konstruktion verwendet - signifikant überlegen ist.

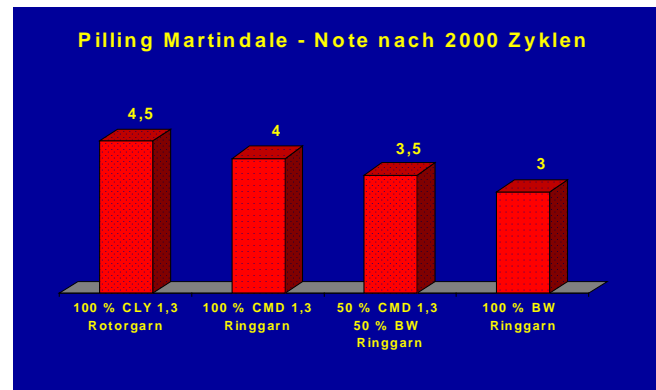


Abb. 9. Lyocell-Baumwolle-Systemmischungen: Gewebevergleich – Körper 2/1, Nm 50/1: Pilling.

## Viscose / Lyocell Mischungen

Eine interessante Anwendung von Lyocell ist mit Sicherheit in der Mischung Lyocell mit Viscose zu sehen. Durch die Beimischung von Lyocell zu regulärer Viscosefaser werden sämtliche textiltechnischen Parameter, die für die Verarbeitung bzw. für den Endverbraucher wichtig sind, signifikant verbessert. Als Beispiel möchte ich mit einem Vergleich von Ring- und Rotorgarnen beginnen. Das Mischungsverhältnis wurde auch hier mit 70 % Viscose und mit 30 % Lyocell gewählt.

### Garnwerte

Bereits in der Spinnerei zeigt sich ein deutlicher Einfluss der beigemischten Lyocellfaser. Beginnend von der Spinnstabilität bis zu den Garneigenschaften, kann man den positiven Einfluss von Lyocell beobachten. Als Beispiel werden die Daten von 100 % Viscose, der Viscose/Lyocell-Mischung und 100 % Lyocell gegenübergestellt. Die Garnfestigkeiten demonstrieren hervorragend den positiven Einfluss von Lyocell.

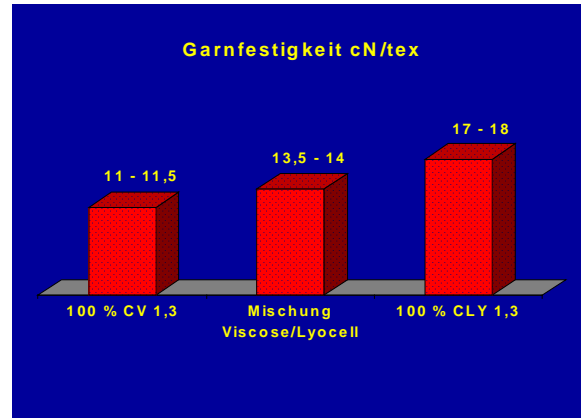
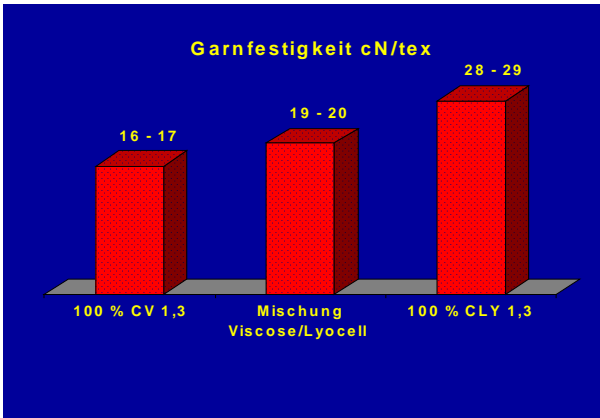


Abb. 10. Viscose/Lyocell Mischungen: Garnfestigkeit. a) Ringgarn Nm 50/1; b) Rotorgarn Nm 60/1.

### Dehnung

Die Rotorgarndehnungen liegen bei den Mischungen naturgemäß etwas niedriger. Deshalb, weil natürlich Lyocell eine signifikant

geringere Dehnung als Viscose aufweist, wobei zwischen 100 % Lyocell und der Viscose/Lyocell-Mischung fast kein Unterschied besteht.

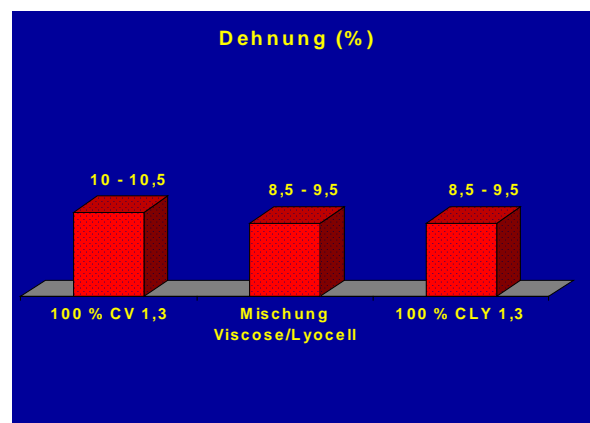
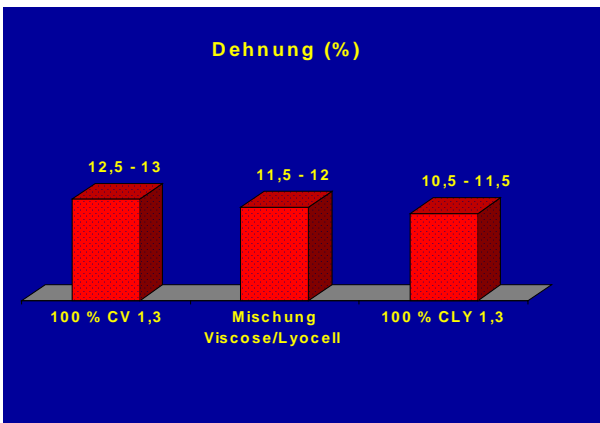


Abb. 11. Viscose/Lyocell Mischungen: Dehnung. a) Ringgarn Nm 50/1; b) Rotorgarn Nm 60/1.

### Uster – Gleichmäßigkeit / U-CV

Die Garngleichmäßigkeit von Ringgarnen aus der Viscose/Lyocell-Mischung unterscheidet sich nicht von 100 % Viscose bzw. 100 %

Lyocell. Bei den Rotorgarnen liegen Viscose und die Viscose/Lyocell-Mischung graduell günstiger als 100 % Lyocell.

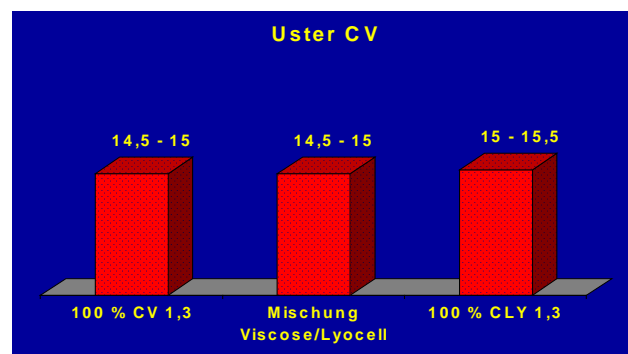
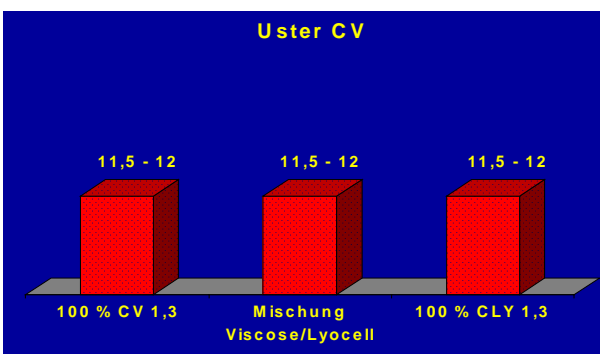


Abb. 12. Viscose/Lyocell Mischungen: Uster Gleichmäßigkeit. a) Ringgarn Nm 50/1; b) Rotorgarn Nm 60/1.



### Imperfektionen

Für die Imperfektionen möchte ich stellvertretend die Dickstellen als Vergleich heranziehen. Hier zeigt sich, dass bei Ringgarnen die Dickstellen zugunsten der Viscose/Lyocell-Mischung ausfallen. Bei den Rotorgarnen ist zwischen 100 % Viscose und

der Viscose/Lyocell-Mischung kein signifikanter Unterschied zu erkennen, hingegen ist 100 % Lyocell deutlich ungünstiger. Die Dünnstellen und Noppen sind zwischen den verglichenen Provenienzen nicht verschieden.

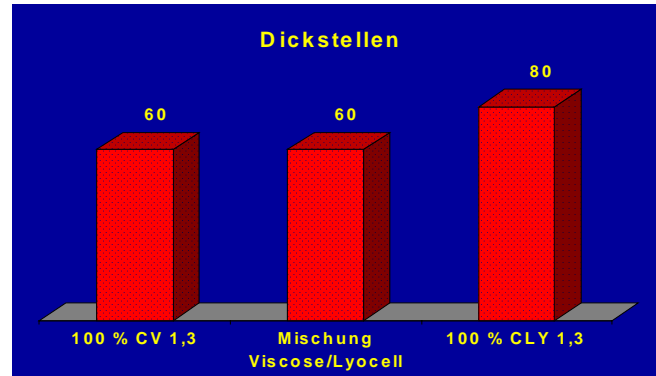
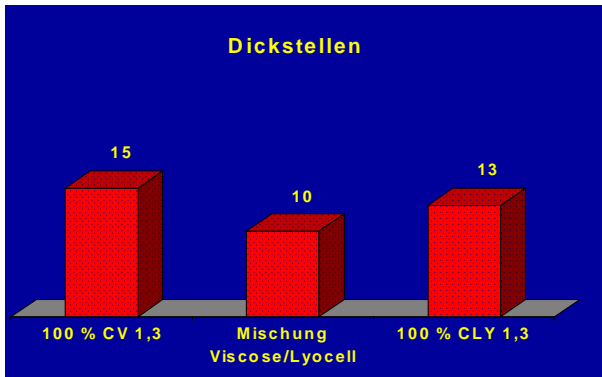


Abb. 13. Viscose/Lyocell Mischungen: Dickstellen. a) Ringgarn Nm 50/1; b) Rotorgarn Nm 60/1.

### Classimat

Der Classimatwert von der Viscose/Lyocell-Mischung ist im Ringgarn signifikant günstiger

und unterscheidet sich im Rotorgarn nicht von 100 % Viscose.

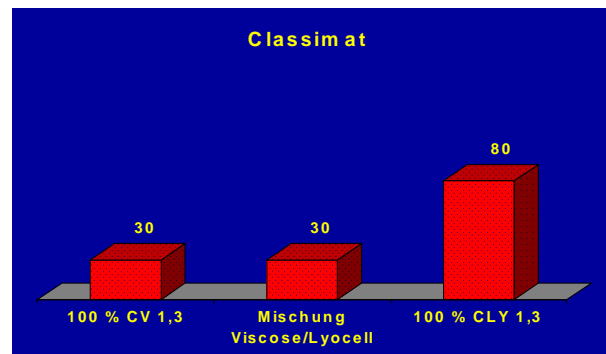
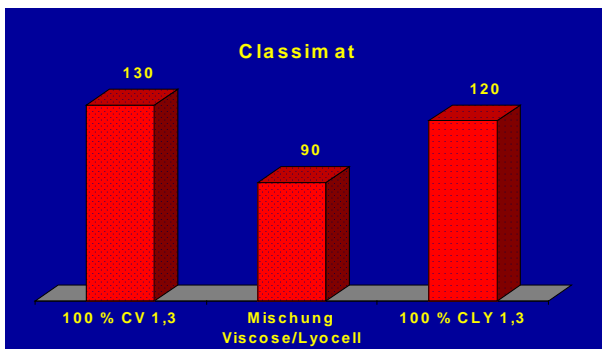


Abb. 14. Viscose/Lyocell Mischungen: Classimat. a) Ringgarn Nm 50/1; b) Rotorgarn Nm 60/1.

### Kreppgarne

Überzeugend ist der Vorteil von der Viscose/Lyocell-Mischung bei der Herstellung von Kreppgarnen zu dokumentieren. In einer Versuchsreihe wurden Garne in Nm 34/1 mit  $\alpha$  230 mit zwei unterschiedlichen Ringläufergeschwindigkeiten hergestellt. Als Vergleich wurde Normalviscose 1,3 dtex sowie Modal 1,3 dtex zu Viscose/Lyocell-Mischung herangezogen.

### Garnfestigkeiten

Es ist überraschend, dass die Garnfestigkeiten bei der Viscose/Lyocell-Mischung der Festigkeit von Garnen aus 100 % Modal deutlich überlegen sind, obwohl die Einzelfaserfestigkeit dieser Mischung signifikant unter der Faserfestigkeit von Modal liegt.

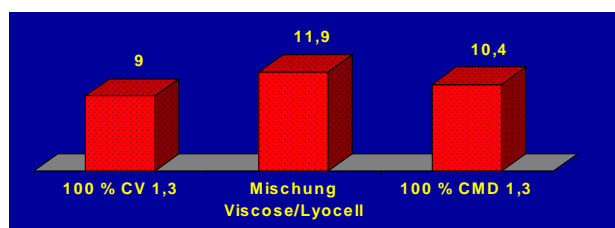
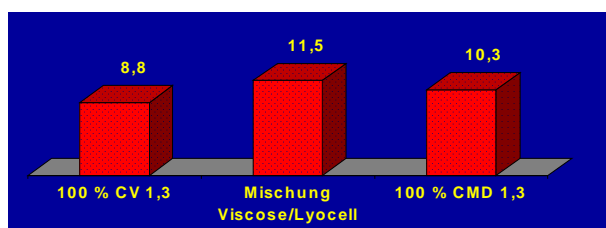


Abb. 15. Viscose/Lyocell Mischungen: Garnfestigkeit, Krepp Nm 34/1. a) 31 Rglfm/s; b) 38 Rglfm/s.

### Dehnung

Auch hier überrascht, dass die Garndehnung durch die Lyocell-Beimischung, speziell bei der höheren Liefergeschwindigkeit, das Niveau der

niedrigeren Produktionsgeschwindigkeit beibehält, wohingegen bei Viscose und Modal eine Reduktion der Dehnung zu verzeichnen ist.

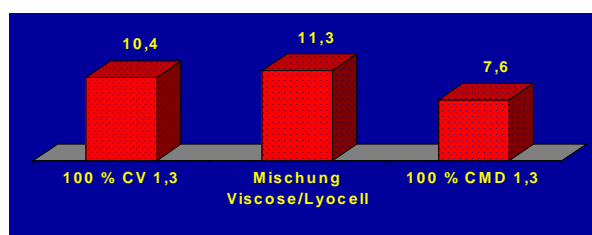
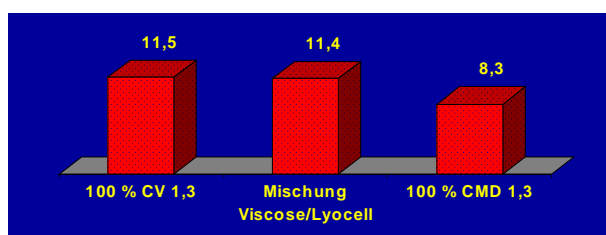


Abb. 16. Viscose/Lyocell Mischungen: Dehnung, Krepp Nm 34/1. a) 31 Rglfm/s; b) 38 Rglfm/s.

### Uster – Gleichmäßigkeit

Die Garngleichmäßigkeit von Modal zeigt die günstigsten Werte und verändert sich auch mit hoher Ringspinnengeschwindigkeit nicht.

Die Viscose/Lyocell-Mischung liegt auf einem leicht schlechteren Niveau, verändert sich aber auch bei höheren Ringspinnengeschwindigkeiten kaum, wohingegen die normale Viscose in der Garngleichmäßigkeit abfällt.

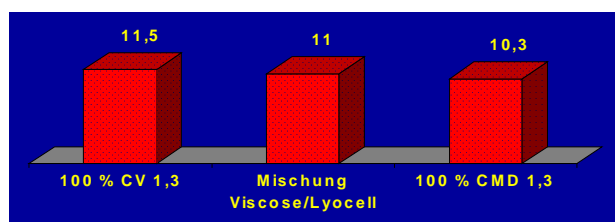
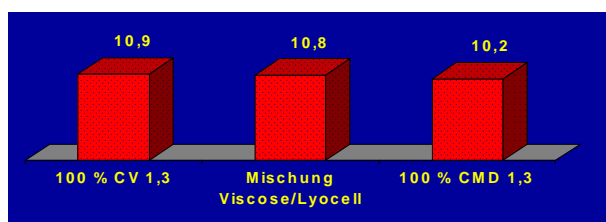


Abb. 17. Viscose/Lyocell Mischungen: Uster Gleichmäßigkeit, Krepp Nm 34/1. a) 31 Rglfm/s; b) 38 Rglfm/s.

### Imperfektionen

Die Imperfektionswerte sind grundsätzlich als gut zu bezeichnen. Ich möchte die Noppen stellvertretend für alle Imperfektionen demonstrieren, da sich die Dünnstellen nicht signifikant unterscheiden und die Anzahl der Dickstellen einen vergleichbaren Wert wie die

Noppen aufweist. Auch hier zeigt sich, dass die Viscose/Lyocell-Mischung im Vergleich zu normaler Viscose und Modal sehr positiv beurteilt werden kann.

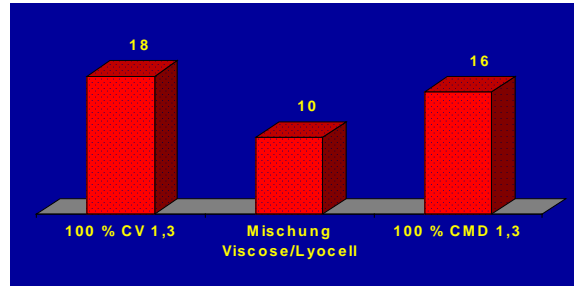
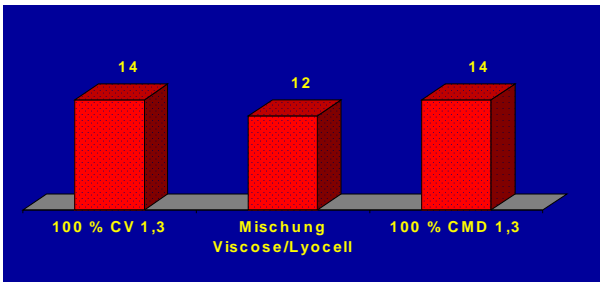


Abb. 18. Viscose/Lyocell Mischungen: Noppen, Krepp Nm 34/1. a) 31 Rglfm/s; b) 38 Rglfm/s.

Betrachtet man all diese Ergebnisse, so wird man feststellen, dass speziell die Viscose/Lyocell-Mischung im Bereich der hochgedrehten Garne eine Bereicherung für die Produktpalette darstellt, da auch neue Endanwendungen mit höheren Drehungsbeiwerten als bisher üblich möglich sein werden, wodurch neue Optiken und Griffvarianten realisiert werden können.

### Washable Rayon

Im Rahmen eines Projektes für die USA (Washable Rayon) haben wir eine klassische Viscose-Druckware, wie sie heute im DOB-Bereich eingesetzt wird, zur Viscose/Lyocell-Mischung verglichen. Die Konstruktion wurde in Leinwandbindung bei einem Flächengewicht von 130 g/m<sup>2</sup> gewebt.

<b>Bindung:</b>	<b>Leinwand</b>
<b>Flächengewicht:</b>	<b>130 g/m<sup>2</sup></b>
<b>Kettdichte</b>	<b>294 Fd/cm</b>
<b>Schußdichte</b>	<b>243 Fd/cm</b>
<b>Kettgarn</b>	<b>Nm 50 OE</b>
<b>Schußgarn</b>	<b>Nm 50 Ring</b>

Abb. 19. Viscose-Lyocell-Mischungen: Washable Rayon Gewebekonstruktion.

Durch diesen Vergleich soll gezeigt werden, welche Vorteile durch eine Beimischung von 35 % Lyocell zu Lenzing Viscose ermöglicht werden. Der Ausrüstungsgang der Qualitäten wurde dem von 100 % Lenzing Viscose untergeordnet, d.h. die Kosten der Ausrüstung

bleiben auf dem Niveau von Geweben aus 100 % Viscose.

Als Ergebnis dieser Entwicklungen zeigt sich, dass die Viscose/Lyocell-Mischung neben den besseren Gebrauchstüchtigkeiten einen deutlich schöneren Griff als 100 % Viscose aufweist.

Stellvertretend für die mechanischen Gebrauchstüchtigkeiten möchte ich die Gewebefestigkeit und das Pillverhalten demonstrieren.

Die Gewebefestigkeit spricht naturgemäß leicht zugunsten von der Viscose/Lyocell-Mischung, das Pillverhalten liegt jedoch signifikant günstiger als bei 100 % Viscose.

Besonders hervorheben möchte ich jedoch neben den mechanischen Gebrauchstüchtigkeiten die Eigenschaften, die im nassen Zustand von besonderer Bedeutung sind, wie den Längenverlust, der in der Ausrüstung zwischen der Rohware und der Fertigware auftritt, sowie die Maßänderung der fertig ausgerüsteten Ware nach 25 Wäschen.

Nicht unerwähnt soll bleiben, dass durch die höhere Festigkeit der Fasermischung eine deutlich höhere Prozesssicherheit gegeben ist und der Anteil der Minderqualität erheblich reduziert werden kann.

Die Prozesssicherheit ist durch die höhere Zugfestigkeit, eine deutlich höhere Einreißfestigkeit, das bessere Schrumpfverhalten und den geringeren Längseinsprung gegeben.

Wie man sieht, zeigen die vorliegenden Daten signifikante Vorteile für die Viscose/Lyocell-Mischung.

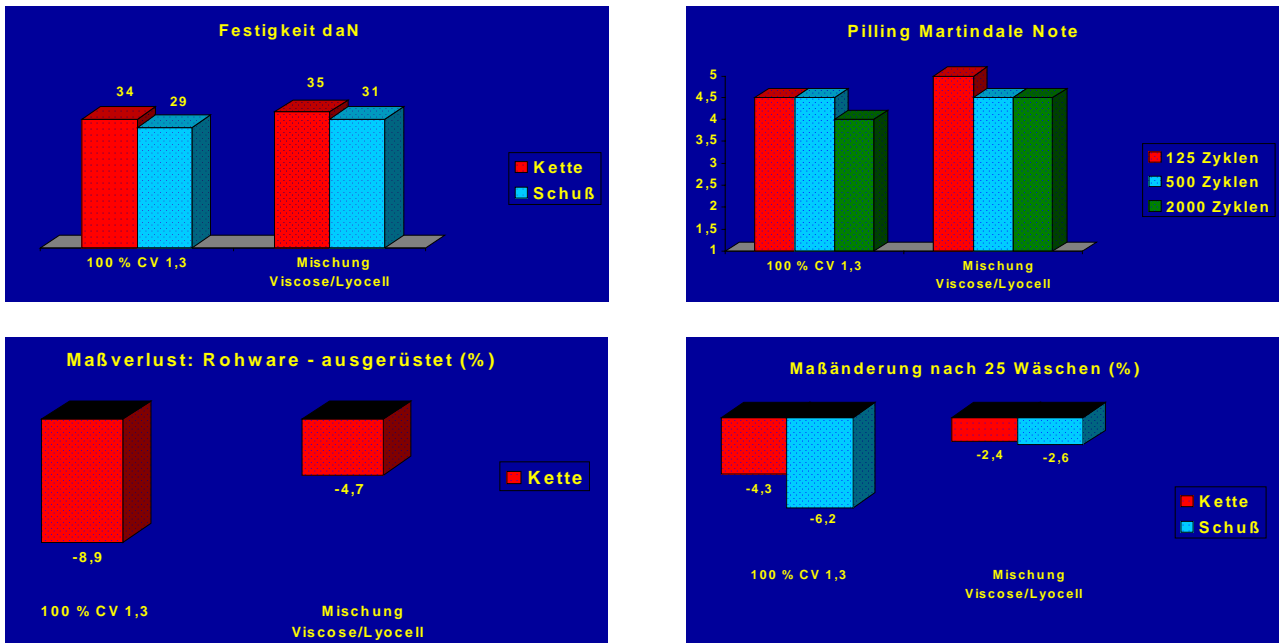


Abb. 20. Viscose-Lyocell-Mischungen: Washable Rayon Gewebekonstruktion.

## Kundennutzen

Mischungen mit Lyocell sind - wie bereits mehrmals angeführt - einfach zu verarbeiten. Ein Maschinenpark, der für die Herstellung normaler cellulosischer Regeneratfasern verwendet wird, erfüllt auch für die Verarbeitung von Fasermischungen die gestellten Anforderungen.

Die guten Faserdaten von Lyocell, eine optimale Fasermischung und entsprechend abgestimmte Konstruktionen bieten eine Reihe von Vorteilen in allen Verarbeitungsstufen.

Von der Spinnerei, wo aufgrund der hohen Festigkeit z. B. auch mit höherer Lieferleistung gefahren werden kann, bis hin zur Weberei, wo Lyocell-Rotorgarne oder deren Mischungen mitunter sogar ohne Schlichte verarbeitet werden können, ergeben sich quantifizierbare Vorteile für die gesamte textile Kette.

Zum Thema „schlichtefreie Rotorgarne“ wird im Anschluss Herr Rosery von der Firma Schlafhorst ausführlich berichten.

Ich möchte aber darauf hinweisen, dass neben dem Entfallen der Schlichtekosten auch ein Vorteil für die Umwelt gegeben ist, da kein CSB bzw. BSB durch Schlichteabbau anfällt. Somit darf nicht nur das Argument der Kosten, sondern auch das Argument der Umweltfreundlichkeit getrost in den Mund genommen werden.

## Zusammenfassung

Zusammenfassend möchte ich die wichtigsten Punkte noch einmal festhalten:

- Lyocellfasern zeichnen sich durch eine Faserfestigkeit aus, die bisher für Zellulosefasern unerreichbar waren.
- Die textilen Eigenschaften von Lyocell sind mit jenen von hochwertigster, langstapeliger Baumwolle zu vergleichen bzw. sind dieser sogar überlegen.
- Die derzeit installierte Kapazität von Lyocell liegt bei ca. 100.000 t. Daraus ist ersichtlich, dass diese Fasergeneration in der Textilindustrie in Zukunft eine universelle Anwendung finden wird, wobei die derzeitigen Hindernisse in den textilen Verarbeitungsstufen ausgeräumt sein werden.
- Lyocell ist ein ausgezeichneter Mischungspartner für nahezu alle am Markt angebotenen Fasertypen. Bei entsprechendem Einsatz und gut gewählten Konstruktionen kann selbst bei einer fibrillierenden Lyocellfaser auf zusätzliche aufwendige Färbe- und Ausrüstungsschritte, wie sie für Lyocell sonst notwendig sind, verzichtet werden.
- Kundennutzen für die Anwender stehen im Vordergrund und werden entsprechend umgesetzt und vermarktet werden.

- Lyocell ist aufgrund der ausgezeichneten Trocken- und Naßfestigkeitseigenschaften bestens geeignet für die neuen Hochleistungstechnologien in der textilen Kette. Hochleistungsgarnherstellung (OE, Air Jet) und Hochleistungswebverfahren, wo sogar auf den Schlichteprozess da und dort verzichtet werden kann, werden für diese Fasergeneration keine Probleme darstellen.
- Eine nicht fibrillierende Lyocellfaser wird in Zukunft unser Faserangebot ergänzen, womit völlig neue Perspektiven von gewünschter Fibrillierung bis hin zu Nicht-Fibrillierung von Textilien eröffnet werden.
- hohe Festigkeit
- exzellente Maßstabilität
- besonderer Griff
- besondere Optik.

### **Danksagung**

Ich möchte mich bei den Firmen Borckenstein, Linz Textil, Wisselink und KBC sowie bei allen Kollegen meiner Abteilung, die bei der Erstellung dieses Vortrages mitgewirkt haben, für ihre Unterstützung bedanken.

## IMPROVEMENTS IN PROCESSING OF TENCEL FIBRES AND FABRICS

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The TENCEL<sup>®</sup> manufacturing process has been in commercial operation for 10 years now and has proved to be very successful technically, economically and environmentally.

TENCEL<sup>®</sup> garments in the market have proved to have an excellent balance of comfort, soft touch and performance. The range of garment types has expanded enormously in this period as the processing technologies have been developed.

Recent advances in fibre crimping are described that have given significant improvements to the performance of the fibre during carding and yarn spinning.

Early advances in the dyeing and finishing of TENCEL<sup>®</sup> were based on the use of enzymes. New, more economical routes have now been developed that can yield TENCEL<sup>®</sup> fabrics with the same comfort and performance attributes. These are outlined in this paper.

### Introduction

In 1992 a new cellulosic fibre was launched commercially under the brand name "TENCEL<sup>®</sup>". It was the first major new fibre for 30 years and was generically classified as Lyocell. It is 100 % natural in origin as it is made from wood pulp and is of high purity and fully biodegradable. It has superior textile performance and out-performs cotton and viscose in many applications. TENCEL<sup>®</sup> garments are comfortable to wear because they are breathable and water absorbent.

As with most major new fibres, there have been many new challenges that need to be met before the fibre can become widely used. In this paper I will highlight the main issues that have arisen and summarise the progress that has been made to successfully overcome them.

TENCEL<sup>®</sup> is made by a new process route, and we have needed to learn how to fully exploit its inherent benefits. One key aspect that I will be discussing in this paper is the new fibre crimp route.

The fibre can produce fabrics that have excellent textile performance, but new dyeing/finishing

technology has had to be developed. I will explain the progress we have made.

TENCEL<sup>®</sup> is comfortable to wear but, for this to be of most benefit, we need to deliver this to the market at affordable prices. I will demonstrate the degree to which we are now able to achieve this.

### The new tow wash/crimping process

The TENCEL<sup>®</sup> process route has been well publicised and I will not dwell on it here. In outline, wood pulp is dissolved in NMMO solvent, spun into an aqueous bath, then washed, dried and cut. The solvent is recycled to a very high level of efficiency. Much of the process required new, high technology equipment and procedures and these are now covered by a large number of patents that have been granted worldwide.

This paper will cover one new feature of the TENCEL<sup>®</sup> production route that has not been discussed frequently - the use of a tow route to wash and dry the fibre.

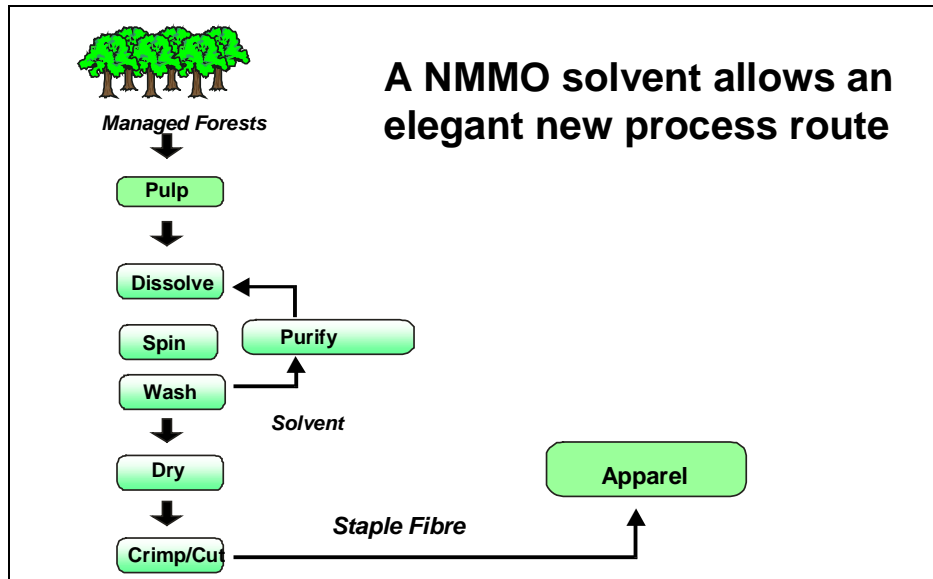


Figure 1. Tencel production route.

Traditional viscose staple fibres are normally cut soon after spinning and then washed and dried as a bed. This can lead to problems in achieving product uniformity, avoiding fibre entanglements and difficulties in product changes.

For TENCEL® we chose to wash and dry the fibre as an uncut tow to achieve uniformity and facilitate good quality control. The tow is then mechanically crimped using a stuffer box crimper to allow easy processing to yarns and non woven webs. This was a pioneering technology for cellulose fibres. The crimped tow is then cut and baled on line.

The expected benefits of this tow route have now been well demonstrated in practice. As well as achieving a uniform and consistent product, the fibres are easily opened with a minimum of entanglements. They give either uniform card webs with a minimum of neps or are readily processed by air laying equipment for non woven webs. Yarn quality is very good in all aspects.

### Improvements in fibre processing characteristics

As expected, further improvements to this route have been requested, the most important being to increase the fibre cohesion. This is particularly important for high speed carding. We quickly demonstrated that increased crimp levels would be beneficial but this posed us

some technical challenges because TENCEL® is not an easy fibre to crimp. Dry cellulose is not thermoplastic so we need to use steam to plasticise it.

Fibre type	Maximum carding speed [m/min]
TENCEL HS260	250+
POLYESTER	200-250
LYOCELL	150-200
VISCOSE	~150

Table 1. Comparative Carding Speeds.

After many years manufacturing experience we have learned how to fine tune the control of the crimping process. Recent technical advances with crimper design and finish selection have lead to major technical advances and, by the end of 2001, we were test marketing our first new high crimp fibre – TENCEL® HS260.

The benefits in terms of maximum card speed were remarkable – it processed smoothly at a very high carding speed on the Thibau card on which the trials were carried out (Table 1). The webs formed in the trials were 30 gsm.

In addition there were other significant benefits such as low fly generation, good web stability and low nep levels. The form of the fibre is very similar to that of polyester staple so blending with that fibre is very efficient.

The TENCEL® HS260 has been launched commercially and customer reaction has been very positive.

The high crimp fibre is also being developed for yarn spinning and results are again very encouraging. Yarn processing and quality improvements are seen in most of the normally monitored characteristics. In Table 2 are the results from the first trial in a commercial mill. The yarn was OE spun to 20Nm using 1.4dtex

fibre. The processing performance was good in all aspects and yarn regularity improved significantly.

Further commercial scale trials are being carried out and we expect to make the fibre commercially available soon.

		TENCEL <sup>®</sup>	TENCEL <sup>®</sup> High crimp
<i>YARN TENSILES</i>	TENACITY (cN/tex)	20	20
	EXTENSION (%)	7.8	8.4
	CV% (TENACITY)	7.9	5.8
<i>REGULARITY</i>	%CV (UT3)	11.1	10.2
<i>IMPERFECTIONS (per 1000m)</i>	THICK PLACES +50%	2	1
	THIN PLACES -40%	21	12
	THIN PLACES -50%	1	0
	NEPS +200%	3	0

**Table 2.** Yarn quality data – commercial mill.

### Advances in dyeing and finishing technology for TENCEL<sup>®</sup> fabrics

In this section of the paper, I will discuss the technologies that have played the most important part in the market development of TENCEL<sup>®</sup> - dyeing/finishing of fabrics and garments.

#### The TENCEL<sup>®</sup> touch is born

TENCEL<sup>®</sup> pioneered the soft, peach touch aesthetic in denim in Japan in 1992/94. Not only was the peach touch very popular, but the garments that were on the market were fashionable in appearance and very comfortable to wear. They also proved to be durable in use. This success with denim was replicated worldwide in the following years.

The big challenge that followed from this was to expand the processing range beyond denim. There was a very strong customer demand for the TENCEL<sup>®</sup> touch to become available in a much wider range of apparel – and at affordable prices. The market growth of TENCEL<sup>®</sup> has been very significantly effected by the rate of technical progress in developing economic processes to make soft touch fabrics.

### Development challenges

Early peach touch products required expensive process routes that, in many cases, required specialist equipment. This particularly applied to piece dyed fabrics.

The development of an understanding of the process fundamentals has enabled us to significantly expand the process routes and reduce the costs. The key to this has been learning to manipulate the fibrillation of the fibre during the dyeing/finishing process.

As is now well known, fibrillation occurs during the wet abrasion of the fibre and is the property that gives the characteristic peach surface to the fibres. However, incorrect control of the fibrillation can give unwanted effects to the fabric appearance or handle.

The use of enzymes was the key to early success. Enzymes were used to clean the fabric surface and also to soften the fabric.

Following these early discoveries, we expanded the range of processing machines that could be used to make commercial quality products – all based on the use of enzymes. Garment washing and dyeing was the next stage in the development since they were closest to the equipment used in denim processing. This was extended to piece dyeing by the use of the special Nidom machines in Japan and then to air



jet dyeing machines worldwide. Tumblers were also introduced for piece dyed products worldwide.

### **Manipulation of fibrillation**

So let us consider the basic principles to achieve a 'peach' aesthetic by the enzyme route.

Firstly you must remove the surface fibres/hairs on the fabric since it is these that will give unsightly pills when the fibres are fibrillated. Next you fibrillate the fabric surface to give the peach touch. Then you tumble the fabric to complete the clean up and give bulk and fullness to the fabric.

The following is a typical process route using enzymes.

- In the pre fibrillation stage, the surface fibres are fibrillated by wet abrasion in either garment or jet processing equipment.
- Enzymes are then used in similar machines to remove the surface fibres and fibrils.
- The fabric is then subjected to wet abrasion – possibly during the dyeing process – during which the surface fibrillation is generated. Because the long surface hairs were removed in the earlier steps, the fibrils formed by this step are held close to the fabric surface so that pilling is avoided.
- A tumbling stage is then used to develop further bulk and softness in the fabric.

Different softener types can be used to refine the aesthetic and easy care resins are sometimes used to optimise appearance retention.

There are of course many variations on the theme of this route – each developed to suit market needs and customers' dye house facilities and expertise. A whole new industry has been developed over the last 10 years based on the above principles and a very wide range of attractive garments have been successfully delivered to the market.

### **The next generation of finishing process routes**

In order to enable TENCEL<sup>®</sup> to reach its true market potential, further improvements in dyeing/finishing were called for. Enzymes are expensive products and need careful process control during use. Furthermore long process

times are required (~14 hours on a jet) and this can restrict the total capacity of some dye houses. The careful process control requirements also restrict the number of dye houses that can successfully process the fabrics.

We therefore need more economical alternatives routes that will give the same attractive aesthetics, comfort and performance.

One successful approach to this that we have developed is to use alternate chemicals instead of enzymes. I will outline our progress in this below.

The first of these alternative routes is to provide chemical energy by a combination of oxidative degradation and causticisation. The oxidative degradation is brought about by hydrogen peroxide treatment during desizing and this is followed by a causticisation treatment that completes the process. The pre-treated fabrics can then be dyed in an air jet, garment machine or in pad dyeing. These pre-treatments weaken the surface fibres/hairs on the fabric so that they are readily removed by the mechanical action in the dyeing and tumbling stages.

A variation of this route is to apply the caustic and peroxide in a single stage then to pad batch (PB) the fabric to allow the degradation process to occur. The pre-treated fabric can then be dyed/tumbled etc as above.

A third route we have developed is called 'Resin Beat'. This process exploits the brittleness of surface hairs/fibrils after resination of fabric.

Fabric is allowed to fibrillate during a normal dyeing and finishing process and then is given an after treatment with an easy care resin. The fabric is then tumbled and the mechanical action causes the surface pills to fall off the surface of the fabric.

The resin beat process yields a slightly different 'peach touch' aesthetic to the other routes but it is still very attractive and fabric performance is very good. The fabrics retain their appearance well after wash and wear cycles.

The cost benefits of these new routes can be appreciated by comparing the typical relative processing times of the different routes in the following table. We have taken the process time to make a soft touch cotton fabric as the base line of 100.

<b>Process route</b>	<b>Relative process time</b>
<i>Cotton - jet dye</i>	100
<i>Tencel on Nidom</i>	240
<i>Enzyme by air jet</i>	210
<i>Oxidative degradation</i>	120
<i>Oxidative degradation (PB)</i>	115
<i>Resin beat</i>	105

**Table 3.** Reductions in dyeing/finishing process time.

These new technologies are now gaining acceptance in the market and we are increasingly confident that they will have a major impact on the commercial success of TENCEL® in the coming years.

## Conclusions

The new technologies in TENCEL® fibre manufacture and the new performance characteristics of the fibre have opened up a large range of new product opportunities.

The TENCEL® tow process route offers a new range of product forms for cellulose fibres. Modifications to the fibre crimp level and finish type will enable us to readily customise the fibre for a wide variety of applications.

The high strength of the TENCEL® fibre combined with its fibrillar nature allows a new family of dyeing/finishing techniques to be used to broaden the range of comfortable fabrics that perform well in use. The latest advances in dyeing/finishing technologies should help to unlock the large market potential for the fibre.

## LENZING LYOCELL® FILL – DIE NEUE FÜLLFASER FÜRS BETT

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In den letzten Jahren haben Füllfasern einen enormen Stellenwert im Bettenbereich erhalten. Aufgrund moderner Heizsysteme nimmt die Bedeutung der Wärmeisolation ab, wohingegen die Eigenschaften des Feuchtigkeitstransportes bzw. des Feuchtigkeitsmanagements an Wichtigkeit gewinnen. Überraschenderweise wurde gefunden, dass sich die Cellulosefaser Lenzing Lyocell als Füllmaterial dazu sehr gut eignet, da es eine ausreichende Bauschkraft und damit

Wärmeisolation besitzt und durch einen exzellenten Feuchtigkeitstransport besticht. Es werden typische Füllmaterialien wie Daune, Wolle und vor allem Polyester der neuen Faser Lenzing Lyocell® FILL gegenübergestellt. Dabei wird der potentielle Einsatz von Lyocell in 100% und Mischungen bei kardierten Vliesen in Steppdecken, verfestigten Vliesen bei Matratzen und Faserbällchen für Kissen vorgestellt.

### Einleitung

Die Entwicklung von Füllfasern der neuesten Generation ist eine enorme Herausforderung, zumal an diese vielfältigste Ansprüche gestellt werden. Neben der Isolationswirkung, sollte der Artikel eine gewisse Bauschigkeit, kombiniert mit Weichheit, aufweisen. Zudem soll das Füllmaterial ausreichende mechanische Stabilität zeigen. Obwohl Steppbetten eigentlich (noch) nicht zu Hygieneartikeln zählen, fordert der Konsument mit Recht ein sauberes Produkt. Dies bedeutet den Einsatz reiner Materialien. Zusätzlich sollte der fertige Artikel nach Möglichkeit auch noch waschbar konzipiert sein. Dem Komfortfaktor ist im „feel well“-Zeitalter ein immer bedeutenderer Stellenwert einzuräumen. Das bedeutet, dass neben ausreichenden Isolationswerten auch das Feuchtigkeitsmanagement optimal erfüllt sein muss.

Im letzten Jahr wurde die neue Faserinnovation Lenzing Lyocell® FILL – in silikonisierter Form mit 60 mm Stapellänge – vorgestellt. Diese Faser erfüllt obiges Anforderungsprofil und findet mittlerweile im Markt schon sehr guten Anklang. Außerdem hat die europäische Umwelt-Kommission im Dezember 2000 dieser neuen Lenzinger Fasertechnologie den begehrten Umweltpreis verliehen. Diese äußerst saubere

Technologie ermöglicht die Herstellung reiner Fasern aus natürlichem, erneuerbarem Rohstoff und äußerster Reinheit, wie auch die Erfüllung des Ökotex Standards 100 Klasse I beweist.

### Anforderungsprofil einer Füllfaser

Das Anforderungsprofil einer Füllfaser kann aus den gewünschten Eigenschaften der Steppware abgeleitet werden. So muss diese eine entsprechende Bauschigkeit, gute Gebrauchswerte und optimale Komfortparameter aufweisen. Im folgenden werden diese Kategorien und der diesbezügliche Stellenwert von Lenzing Lyocell® FILL diskutiert.

### Bauschigkeit

Die Bauschigkeit des Füllkörpers subsummiert im wesentlichen sein Volumen, die Bauscherholung bei mechanischer Deformation und die resultierende Weichheit des Endproduktes. Übersetzt auf Faserebene ergeben sich die Forderungen nach einer möglichst dreidimensionalen Raumausnutzung der Faser (idealerweise 3D-Kräuselung), einer ausreichenden Elastizität der Faser sowie eines optimal eingestellten Haft-Gleitverhaltens zwischen den Füllfasern.

## Kräuselung – die räumliche Ausdehnung der Füllfaser

Die Bauschigkeit des Füllkörpers wird durch dessen Herstellungsverfahren, die verwendeten Grammaturen, aber auch durch die eingesetzte Faser bestimmt. Auf Faserebene bedeutet dies, dass für die Erzielung einer guten Bauschigkeit bereits die einzelne Faser möglichst dreidimensional den Raum ausfüllt und damit dem Füllkörper an sich Volumen gibt (Abb. 1). Dieser Anforderung wird Lenzing Lyocell® FILL aufgrund des patentierten Herstellungsverfahrens (Patentnummer: AT 402.741; EP 0797696; US 6.117.378) gerecht.



Abb. 1. Kräuselung Lenzing Lyocell® FILL 6,7/60 mm.

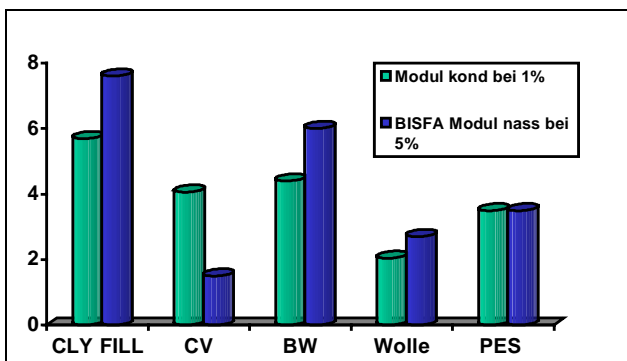


Abb. 2. Vergleich der Moduli.

## Elastizität

Für den Erhalt der Bauschigkeit (Bauschelastizität) muss die Füllfaser ihre räumliche Ausdehnung auch bei Deformation und Wiederentlastung des Füllkörpers aufrechterhalten. Als gute Näherung kann diese

Materialeigenschaft über den Elastizitätsmodul beschrieben werden.

Es wurden die Elastizitätsmoduli der wichtigsten Fasertypen ermittelt. Untersucht wurden Lenzing Lyocell® FILL 6,7 dtex, Viskose 8,9 dtex, Baumwolle, Wolle, PES Hohlfaser 7 dtex. Im Quervergleich zeigt Lenzing Lyocell® FILL sowohl im trockenen als auch nassen Zustand die höchsten Moduli der betrachteten Fasern und liegt somit auch höher als die für diesen Bereich bisher schwerpunktmäßig eingesetzte Wolle und Polyester (Abb. 2).

## Haft-Gleitverhalten

Das Verhalten bei Deformation und Wiederentlastung wird neben der Kräuselung und Steifheit der Faser auch durch das Haft-Gleitverhalten zwischen den Füllfasern bestimmt. Bei mechanischer Deformation werden die Füllfasern zum Teil ineinander verschoben. Die über die Steifheit der Faser gespeicherte Rückstellenergie kann sich nur dann wieder freisetzen, wenn das Haft-Gleitverhalten der Einzelfasern dies zulässt. Auch die subjektiven Eigenschaften wie Weichheit des Füllmaterials und Griff werden davon mitbestimmt.

Durch eine entsprechende Avivierung, sprich Silikonisierung, der Faser kann das Haft-Gleitverhalten optimal eingestellt werden. Die Prüfung der Wiedererholung eines Füllmaterials und damit der Bauschelastizität zeigt die Wirkung dieser Avivierung, wie Abbildung 3 zeigt. Für die Prüfung wurde 3 g Vlies in einem Messzylinder mit einem Gewicht von 1 kg 15 Minuten lang belastet und anschließend wieder entlastet.

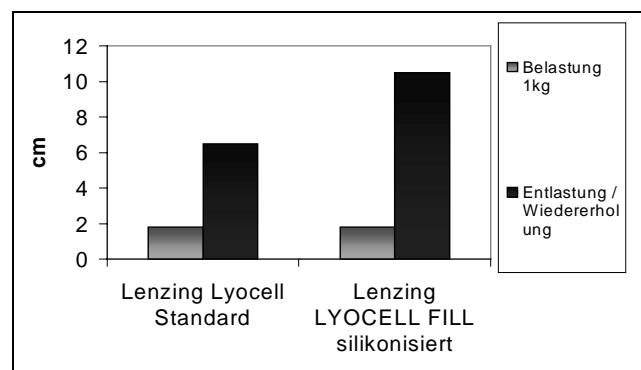


Abb. 3. Wiedererholung von Vliesen bei mechanischer Belastung.

Zusammengefasst zeigt Lenzing Lyocell® FILL hinsichtlich ihrer mechanischen Eigenschaften sehr gute Grundvoraussetzungen für den Einsatz als Füllfaser. Ein praktischer Vergleich anhand

von Steppdecken zeigt, dass eine Füllung mit 100% Lenzing Lyocell® FILL mit Naturfasern (Wolle und Seide) vergleichbare Volumina ergibt.




100% Seide 0,48kg/m <sup>2</sup>	100% Wolle 0,57kg/m <sup>2</sup>	100% Lenzing Lyocell® FILL 0,52kg/m <sup>2</sup>
		

Abb. 4. Vergleich der Deckenvolumina von Füllungen aus Seide, Wolle, Lyocell.

## Gebrauchswerte

### Zigarettenbrenntest

Um den immer strenger werdenden Vorschriften genüge zu tun, hat die Firma Hefel an den Steppdecken mit 100% Lenzing Lyocell® FILL und eingehüllt in ein Inlett aus 100% Lenzing Lyocell® MICRO an den Steppdecken Opal (1 Wärmepunkt), Jade (4 Wärmepunkte) und am Kissen Onyx den Zigarettenbrenntest am ITF durchführen lassen. Diese Produkte haben den Zigarettenbrenntest gemäß „Decret no 2000-164 du 23 fevrier 2000 suivant les normes NF EN 12952“ bestanden.

### Waschbarkeit

Durch die immer häufiger auftretende Hausstauballergie und selbstverständlich auch aus Hygienegründen wird vermehrt im Konsum aber vor allem im Objektbereich die Waschbarkeit von Steppdecken gefordert.

Die Haushaltswäsche gestaltet sich mitunter schwierig, da oftmals das Füllvolumen der Waschmaschine nicht ausreicht, um beispielsweise Decken mit mehr als 3 Wärmepunkten waschen zu können. Vergleicht man nun Steppdecken mit 100% Lenzing Lyocell® FILL, 50% Lenzing Lyocell® FILL / 50% Polyester Hohlfaser 7dtex und 100% Polyester Hohlfaser 7dtex mit jeweils 3 Wärmepunkten, so zeigt die Steppdecke aus 100% Lenzing Lyocell® FILL nur eine sehr eingeschränkte Wasch- und Vliesstabilität (verliert nach 5 Wäschen ca. 50% an Volumen), während die Vliesstabilität der Mischung mit

Polyester vergleichbar mit der Steppdecke aus 100% Polyester ist. Durch Mischung von Lenzing Lyocell® FILL mit Polyester kann ein mit 100% Polyester vergleichbares Bausch- und Waschergebnis erzielt werden.

Für den Objektbereich wurde gemeinsam mit der Firma Hefel und der Firma Wozabal ein Vergleichstest von Steppdecken im industriellen Maßstab durchgeführt. Zielrichtung war die Entwicklung einer atmungsaktiven Steppdecke für Krankenhäuser und Pflegeheime. Dabei wurden eine derzeit im Einsatz befindliche Steppdecke aus 100% PES mit wiederum einer 50% Lenzing Lyocell® FILL / 50% Polyester – Mischung verglichen und insgesamt 50 mal gewaschen. Die optische Beurteilung zeigt, dass die Lyocell-Mischung nach 50 Wäschen die gleiche Vliesbeständigkeit aufweist, wie 100% Polyester. Auch das Volumen der beiden Steppdecken (Abbildung 5) ist vergleichbar.

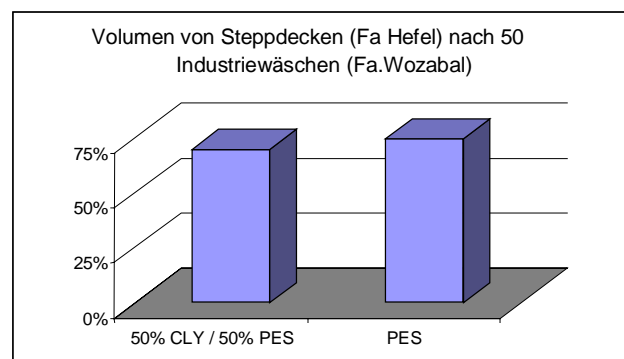


Abb. 5. Deckenvolumen nach Industrierwäsche.

**100% PES hohl 7dtex**  
0,65kg/m<sup>2</sup>



**50% Lenzing Lyocell® FILL**  
50%PES 0,78kg/m<sup>2</sup>



**Abb. 6.** Vergleich der Deckenvolumina von Füllungen aus 100% PES und Mischung PES 50% / Lenzing Lyocell® FILL 50%

**Fazit:** Steppdecken in einer Lenzing Lyocell® FILL / Polyester - Mischung können sowohl industriell als auch im Haushalt problemlos gewaschen werden, behalten weitgehend einen angenehmen Griff und zeigen zudem optimale physiologische Eigenschaften.

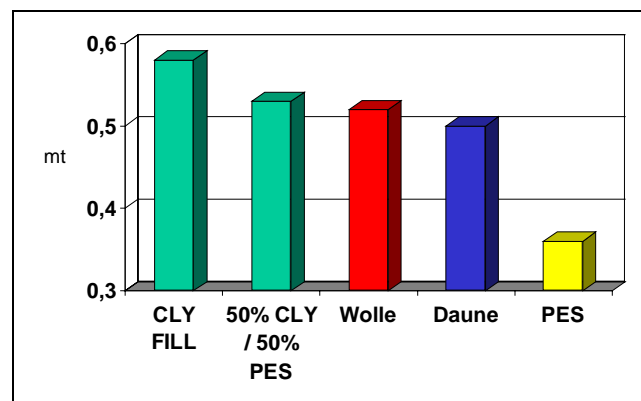
### Komfort – Physiologie

Die ursprüngliche Aufgabe einer Steppdecke, die Wärmeisolation, wird im wesentlichen von allen Produkten erfüllt. Moderne Heizsysteme und damit ausgeglichene Raum-Temperaturen im Schlafzimmer (auch im Winter) relativieren die Wichtigkeit diese Eigenschaft. Beachtenswert ist aber die Tatsache, dass der menschliche Körper während des Schlafes durchschnittlich 0,4 l Feuchtigkeit abgibt, wobei der Großteil in Form von „insensiblen“ Schwitzens als Dampf über die Körperoberfläche abgegeben wird. Der Schlafkomfort wird daher entscheidend durch das Feuchtigkeitsmanagement der Bettdecke bestimmt. Dem folgend spielt die Feuchtigkeitsaufnahme des Füllmaterials und der Feuchtigkeitstransport durch das Füllmaterial eine wesentliche Rolle bei der Auswahl des Füllmaterials.

### Feuchtmanagement

Im Schlafzustand ist der Feuchtigkeitstransport in erster Linie auf die Dampfphase beschränkt. Daher ist vorerst der Abtransport der Feuchtigkeit und damit der Wasserdampftransport durch die Bettdecke zu beachten. Dies kann mittels des Wasserdampfdurchgangswiderstandes eines Füllmaterials gekennzeichnet werden. Als normierte Größe wird dazu der

Wasserdampfdurchgangsindex  $i_{mt}$  (ISO11092) herangezogen, wobei höhere Werte bessere Durchgangswerte bedeuten. Abbildung 7 zeigt dazu die Werte typischer Steppdeckenfüllungen. Untersucht wurden Vliese kommerziell erhältlicher Steppdecken.



**Abb. 7.** Wasserdampfdurchgangsindex  $i_{mt}$ .

So wie beim Wasserdampfdurchgangsindex schneidet Lenzing Lyocell® FILL auch bei anderen physiologischen Parametern wie Kurzzeitwasserdampfaufnahmefähigkeit (ISO-11092) und Feuchtigkeitsausgleichskennzahl am besten ab, so dass Lenzing Lyocell® FILL als der Feuchtigkeitsmanager bezeichnet werden kann. Auch die Mischung von Lenzing Lyocell® FILL mit Polyester zeigt nach wie vor hervorragende physiologische Werte.

Zusammenfassend kann gesagt werden, dass 100% Lenzing Lyocell® FILL hervorragende physiologische Eigenschaften aufweist und wie zu erwarten, die Gebrauchswerte durch Beimischung von Polyester noch verbessert werden.

## Verarbeitungstechnologien

In Bettwaren finden zum überwiegenden Teil zwei Arten von Fasergebilden Einsatz. Diese sind Vliese sowie Faserbällchen. Lenzing Lyocell® FILL ist in beiden Anwendungen einsetzbar und ist durch keine Technologie eingeschränkt.

### Vlies

Die Vliesherstellung nutzt zum überwiegenden Anteil die Krempel und entsprechende Vliesbildner, wie z.B. Kreuzleger. Diese Technologie ist extrem vielseitig einsetzbar und gestattet Lenzing Lyocell® FILL in einer enormen Bandbreite von Grammaturen sowie in verschiedensten Mischungen herzustellen.

Die Verfestigung der Vliese ist unproblematisch und kann mit allen bisher für cellulosische Fasern üblichen Verfahren (Binder, Vernadelung, etc.) durchgeführt werden.

Entsprechend dem Einsatz bzw. den angestrebten Eigenschaften ist für das Vlies - die Vliesorientierung, Schichtung und in der Steppware - die Musterung und die Nahtabstände zu berücksichtigen, da es ansonsten zu Vliesbrüchen bzw. großflächigen Faserverfrachtungen kommen kann.

### Faserbällchen

Für die Erzeugung von Faserbällchen für Bettwaren finden kommerziell zwei Technologien Anwendung. Zum einen ist dies die Krempeltechnologie, bei der im Gegensatz zur normalen Vliesbildung die Einstellungen verändert wurden, so dass die Fasern gerollt und stufenweise zu Faserbällchen geformt und verfestigt werden. Mit dem Krempelverfahren sind Bällchen in 100% Lyocell sowie beliebige Mischungen möglich.

Die zweite Technologie ist das Lufttumblingverfahren (Nowo /FIN - PCT WO 99/36609; finnische Patentnummer: 105571) welches auf einem Stator-/Rotorprinzip beruht. Die resultierende Luftströmung fördert und formt die Fasern in lockere Gebilde, die zunehmend kompakter und damit verfestigt werden.

Die Charakteristik der Faserbällchen (Größe, Form) ist stark von dem Verfahren abhängig, so sind die Nowo Bällchen beispielsweise etwas größer und voluminöser.

**100% PES**

**70% PES / 30% Lenzing  
Lyocell® FILL**  
Krempelverfahren

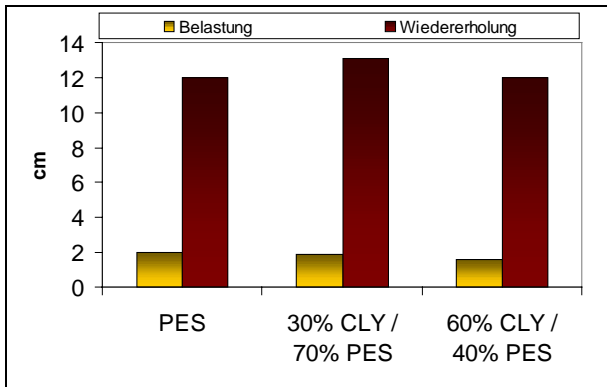
**40% PES / 60% Lenzing  
Lyocell® FILL**  
Lufttumblingverfahren



**Abb. 8.** Optik von Faserbällchen aus PES und PES / Lyocell.

Analog zu Füllkörpern in Vliesform ist die Bauschigkeit bzw. Bauschelastizität von Faserbällchen ein wichtiges Kriterium. Entsprechend dem eingangs beschriebenen Test wurde die Wiedererholung von Faserbällchen aus 100% PES, 30% Lenzing Lyocell® FILL /

70% PES, welche nach dem Krempelverfahren hergestellt wurden, und 60% Lenzing Lyocell® FILL / 40% PES nach dem Lufttumblingverfahren gemessen.



**Abb. 9.** Wiedererholung von Faserbällchen aus PES und PES / Lenzing Lyocell<sup>®</sup> FILL

Die Bauschkraft der Faserbällchen unterschiedlicher Mischungen von Lenzing Lyocell<sup>®</sup> FILL mittels verschiedener Herstellungsverfahren ist durchaus mit 100% PES Bällchen vergleichbar.

## Einsatzgebiete und Zusammenfassung

Lenzing Lyocell<sup>®</sup> FILL und deren Mischungen werden in kardierter Form in Steppdecken, als Faserbällchen primär in Kissen, als Füllmaterial eingesetzt. Die Verwendung bei Polstermöbeln ist derzeit in Erprobung. Auch als Auflagevlies für Matratzen und Matratzenauflagen wird Lenzing Lyocell<sup>®</sup> FILL bereits eingesetzt, so dass wir der Vision des Bettes aus Holz schon einen Schritt näher gekommen sind.

Das Eigenschaftsprofil von Lenzing Lyocell<sup>®</sup> FILL entspricht daher voll dem Trend:

- natürlicher Ursprung
- Reinheit
- Funktionalität hinsichtlich Feuchtigkeitsmanagement
- exzellente Gebrauchseigenschaften speziell in Kombination mit Polyester.

An dieser Stelle bedanken wir uns für die Kooperation bei Firma Hefel, Firma Wozabal und Institut Hohenstein.

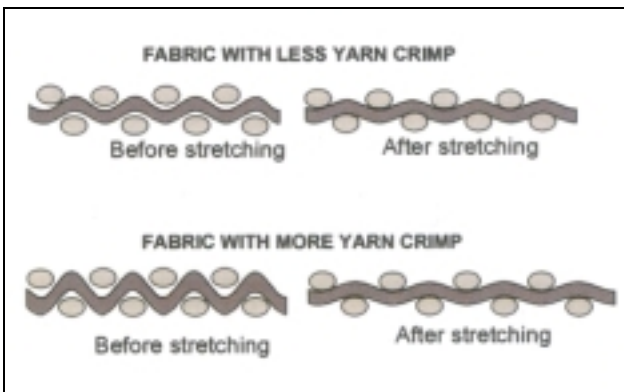


## TENCEL<sup>®</sup> NATURAL STRETCH

Tom Burrow, Bob Morley

TENCEL Ltd., Spondon, Derby DE21 7BP, UK

TENCEL<sup>®</sup> woven fabrics with stretch are now being produced without the addition of any stretch fibres. This has been made possible as a result of the properties of the fibre and our increased knowledge of the textile technology that influences its behaviour. New dyeing and finishing routes have been developed to allow the fabrics to be produced commercially. The stretch that is developed in TENCEL<sup>®</sup> Natural Stretch fabrics is a result of the way the fibres and yarns behave during wet processing. The yarns are crimped to such an extent that they provide the potential for the fabric to increase in length or width. The crimp is set into the yarns giving good recovery from extension.



**Figure 1.** Yarn crimp allows the fabric to stretch.

TENCEL<sup>®</sup> fibres and yarns are not easily stretched under normal wear conditions. TENCEL<sup>®</sup> fibre has a high fibre modulus and resists stretching. The extension at break for dry fibre is typically 12 %. By using the TENCEL<sup>®</sup> Natural Stretch route, fabrics can be produced with up to 25 % stretch.

TENCEL<sup>®</sup> Natural Stretch fabric is easy to stretch allowing freedom of movement and garment comfort. When the load is removed there is rapid recovery of the original TENCEL<sup>®</sup> fabric shape. TENCEL<sup>®</sup> Natural Stretch gives a gentle stretch and not Power-stretch or Support-stretch.

### What is needed to produce TENCEL<sup>®</sup> Natural Stretch

To develop TENCEL<sup>®</sup> Natural Stretch three things are needed. The fabric must be constructed so that it will allow crimp development. The fabric must be processed in such a way that the crimp is allowed to develop. And when the crimp has developed, the fibres need to be set in order to make the stretch permanent. If one of these three elements is missing, then the fabric may not have stretch properties; it may stretch but not recover; or the stretch may not withstand repeated washing. Careful TENCEL<sup>®</sup> loomstate fabric design and appropriate finishing conditions are needed to give optimum stretch and recovery.

TENCEL<sup>®</sup> Natural Stretch is a result of straightening of the yarn crimp within the fabric. High yarn crimp in the finished fabric gives outstanding stretch potential. More yarn crimp means more TENCEL<sup>®</sup> fabric stretch.

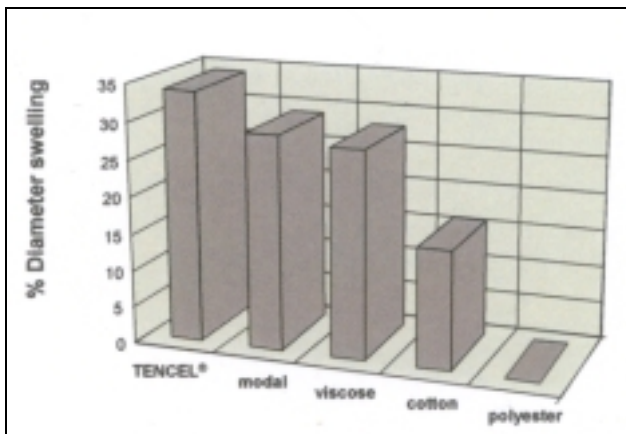
### Fabric construction

If a fabric is required to stretch, then it must be constructed so that it can. The fabric construction determines both the total stretch of the fabric and the balance between warp and weft stretch. If a fabric is to be designed to have weft stretch, then the loomstate fabric should be constructed so that its loomstate width represents the stretched dimension of the final finished fabric. This is the same principle as is applied in producing stretch fabrics with elastane. However, when a fabric is woven with elastane, the width is pulled in as the fabric comes off the loom. With TENCEL<sup>®</sup> Natural Stretch fabrics the width only reduces a small amount from the reed width. A loomstate elastane containing fabric has some stretch properties. A loomstate TENCEL<sup>®</sup> Natural Stretch fabric has virtually no stretch. The stretch is developed during finishing.

## Yarn crimp development

Some yarn crimp is present in all woven fabrics, regardless of fabric construction. The properties of TENCEL<sup>®</sup> allow the development of higher levels of yarn crimp than is possible with other fibres. In most loomstate fabrics, yarn crimp is low and the yarns are in close contact with each other at crossover points. Because there is no space between the yarns, there is little stretch in the loomstate fabric.

Wetting of the loomstate fabric causes fibres and yarns to swell in diameter. The fabric shrinks because the TENCEL<sup>®</sup> yarns push each other apart as they swell and develop a crimped shape. TENCEL<sup>®</sup> yarns do not increase in length due to absorption of water. Neither do they extend much under load because the fibre has a high modulus. Thus, all of the forces that are generated by swelling of the yarns are directed into increasing the yarn crimp.



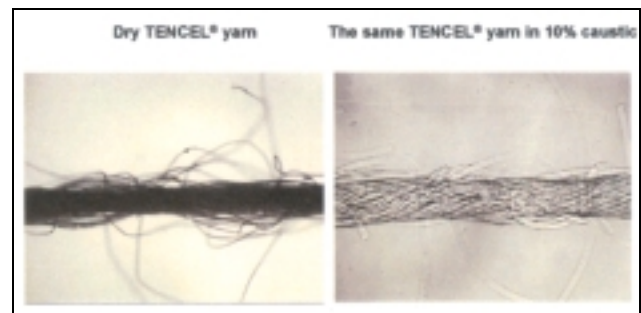
**Figure 2.** Fibre swelling in water: % increase in fibre diameter.

At this stage the fabric still does not have stretch properties. This is because the wet yarns are still in contact with one another so that there is no space available at crossover points for the crimp to be able to straighten. When the fabric is dried, the yarns retain the same shape as they had when they were wet. As a result, spaces develop between the yarns where they cross over. The fabric now has stretch.

## Caustic setting

The amount by which a TENCEL<sup>®</sup> fabric will stretch increases in direct proportion to the amount of yarn crimp. The higher the yarn

crimp, the higher the stretch that can be developed. If there were a way to develop more crimp, then it would be possible to increase the amount of stretch. Because swelling of the fibres and yarns develops the crimp, then greater crimp results from greater swelling. Caustic soda (sodium hydroxide) swells cellulose much more than water does. The diameter of a TENCEL fibre increases by about 35% when it is wetted with water. But when a fibre is wetted with a 10% w/v solution of caustic soda, the diameter can increase by 300%. In a fabric, this level of swelling is not possible because there is insufficient space. The swelling potential therefore translates into an increased force making the yarns crimp.



**Figure 3.** TENCEL<sup>®</sup> yarn swelling in caustic.

To develop maximum stretch in a TENCEL<sup>®</sup> fabric, the fabric is treated with caustic and is allowed to relax. The amount the fabric shrinks is approximately equal to the amount of stretch that will be developed. When the caustic soda solution on the fabric is washed out and neutralised, the fibres that make up the fabric are set into the shapes that they have at that time. This gives the fibres a powerful memory of the unstretched dimensions of the fabric. When a fabric has been treated with caustic soda in this way, the recovery from stretch is much greater. The shape memory that is given to the fibres is not affected by washing of the fabric. The fibres have their memory because of hydrogen bonds formed within the fibre structure. While these bonds could be broken by further treatment with a strong alkali, they cannot be broken by water alone. Thus, each time the fabric is wetted, and allowed to relax, it assumes the stable dimensions it was set at.

## **TENCEL<sup>®</sup> fibre properties**

TENCEL<sup>®</sup> works exceptionally well in the Natural Stretch process because of its high fibre swelling and resistance to caustic treatment. Natural cellulosic fibres do not swell as much as TENCEL<sup>®</sup> in caustic and hence crimp development is not so good. Some other man-made cellulosic fibres cannot be treated with strong caustic solution and hence the swelling cannot be generated.

TENCEL<sup>®</sup> fabrics give good recovery from stretch because the fibre is resilient. This is due to its high fibre stiffness (both dry and wet) that helps TENCEL<sup>®</sup> fabrics to recover their shape. TENCEL<sup>®</sup> fibre also has a high tensile modulus (stiffness) both wet and dry. This stiffness means that TENCEL<sup>®</sup> fibres are not easily deformed within the fabric and can more easily recover their original shape and position. The low modulus of viscose means that it will easily stretch and distort and has limited capacity to recover. Other fibres tend to have an intermediate performance. Despite the high stiffness of TENCEL<sup>®</sup> fibre, TENCEL<sup>®</sup> fabrics are still soft. This is because of the space generated within the fabric by the exceptional TENCEL<sup>®</sup> fibre swelling.

### **Construction economics**

In order to develop weft stretch the fabric must be allowed to shrink in width during processing.

The fabric specification needs to take account of this. The fabric needs to be woven to a width corresponding to the stretched dimension required. The final finished width then corresponds to the unstretched dimension of the fabric. Because warp and weft yarn crimp are interrelated, increases in one may cause reductions in the other. If the warp crimp is less this means that warp shrinkage has been reduced during wet processing. In order to achieve the same picks/cm in the finished fabric, a slight increase in loomstate picks/cm may be necessary. The combined effect of these two points is that the finished fabric metreage per pick inserted in weaving remains unchanged even though picks/cm may have been increased. This is because the changes also mean that shrinkage in fabric length is reduced.

### **Summary**

TENCEL<sup>®</sup> can produce fabrics with a surprising level of stretch and recovery without the need for synthetic or elastane fibres. Changes in fabric construction can be used to provide the scope for increased yarn crimp development and therefore stretch where it is desired. Caustic setting is used to swell the yarns to create yarn crimp and space in the fabric. This maximises fabric stretch as well as enhancing recovery by setting the TENCEL<sup>®</sup> fabric.

## ONLINE QUALITY CONTROL OF VISCOSE BY MEANS OF IMAGE ANALYSIS

S. Jary

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The behavior of solutions or melts during spinning and the characteristics of the resulting fibers are strongly dependent on the content of impurities. Impurities, such as insufficiently dissolved raw material, dirt, or gas bubbles, lead to poor fiber strength or even to a break-off during the regeneration process. For this reason, regular testing prior to spinning is necessary.

Common particle measuring systems for viscose solution quality control do not distinguish between types of impurities, they are off-line, or the viscose has to be further diluted. Therefore, we developed a videomicroscope device. It is possible to integrate this apparatus directly into the pipe

system of the production line. Viscose continuously flows through the cell, the video sequences are transmitted to a monitor or computer. In order to transform the subjective pictures into an objective evaluation, we designed a special image analysis computer program.

Now we are able not only to analyze amount and size of impurities of undiluted viscose, but also to differentiate between impurities of different types by means of an on-line system.

**Keywords:** viscose, particle measurement, image analysis

### Introduction

Quality control of viscose solution concerning impurities is very important with regard to fiber properties: High particle content leads to low fiber strength or even to break-offs and, thus, bad spinning performance.

The two most common methods for viscose evaluation regarding to particle content are working by

- changes of impedance ("COULTER") or
- light blockade (e.g., PAMAS), respectively:

#### *Particle detection by impedance measurement*

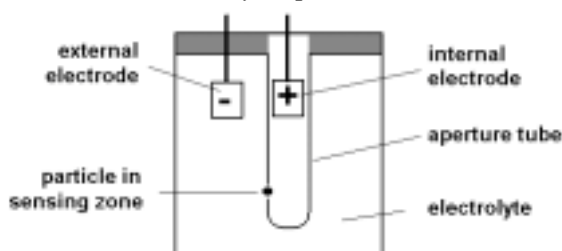


Figure 1. COULTER principle.

The COULTER device consists of two electrodes and a tube, which has an opening. The assembly dips into an electrolyte (e.g., NaOH). Resistance is measured and recorded continuously. Particles, which pass the opening and are not of similar conductivity as the environment, cause a change in impedance according to their three-dimensional size. However, the opening tends to block very easily and gas bubbles are detected as particles as well.

#### *Particle detection via principle of light blockade*

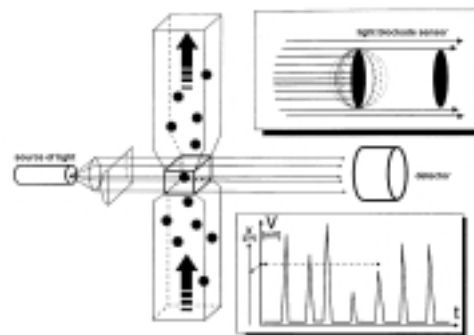


Figure 2. Principle of particle detection by light blockade (Source: GIT Labor-Fachzeitschrift 5/2002).

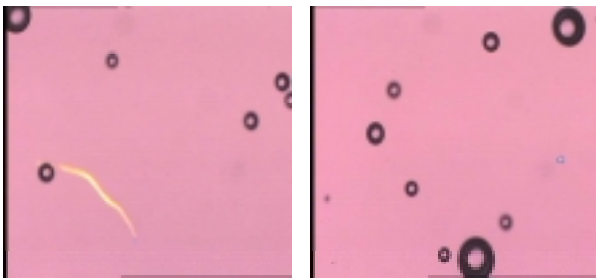
The device – in this case – consists of a light source, a tube, where the medium to be measured is led through, and a detector. If a particle passes the light beam, the detector gives a signal, which is proportional to the diameter. On this basis, particle volume is calculated. Unfortunately, the result is falsified, if the shape of the object is not spherical.

However, there exist several disadvantages for both methods:

- The viscose samples have to be diluted to avoid particle aggregation,
- there is no distinction between types of particles, and
- no online-measurement is possible.

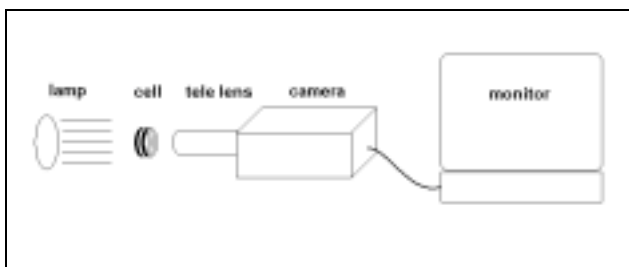
### Image analysis

Upon observing a drop of viscose under a long distance microscope (Figure 3), we had the idea of developing a suitable online method for viscose evaluation, based on image analysis.

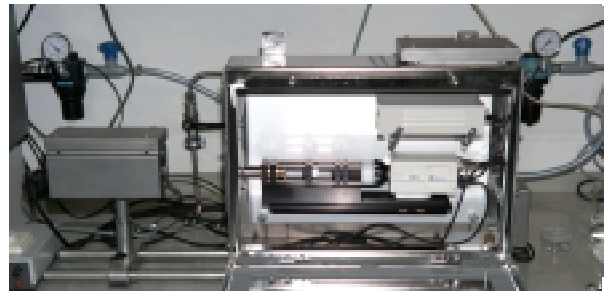


**Figure 3.** Viscose solution (microscopically enlarged).

The core of the videomicroscope assembly developed (Figure 4, Figure 5) is a cell, where viscose is continuously passed through. A camera equipped with tele-optics transmits the video sequences to a monitor.

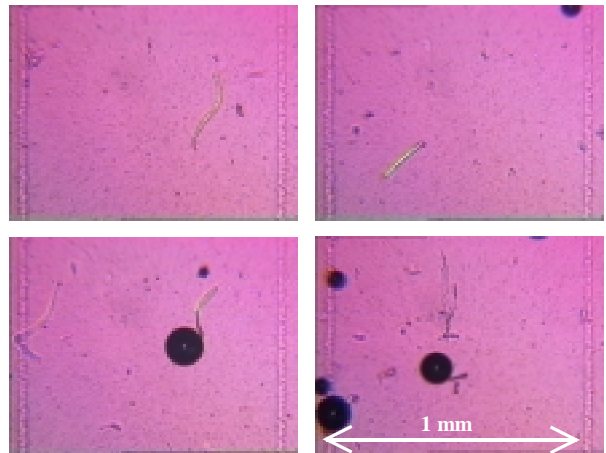


**Figure 4.** Videomicroscope, schematically.



**Figure 5.** Videomicroscope.

However, first trials of the prototype integrated in the production line's pipe system showed the necessity of some further improvements concerning focusing the camera and sealing the cell. After realization, we were able to record well-focused video sequences of viscose solutions enlarged 200 times (Figure 6).



**Figure 6.** Shoots of viscose.

So we reached our first goals:

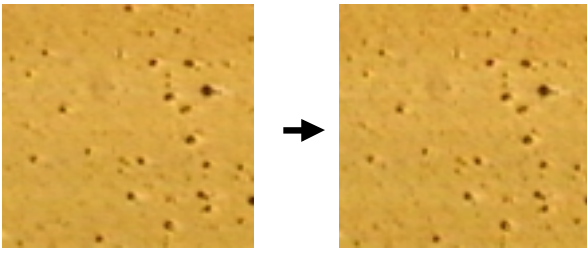
The possibility of:

- continuous control,
- online control, and
- identification of gas bubbles and fibers.

However, without a computer supported analysis, the system was still subjective. Our next objective was to find a suitable image analysis system to evaluate number and size of impurities. The software should be able to distinguish between particle types, and to identify deposits inside the cell.

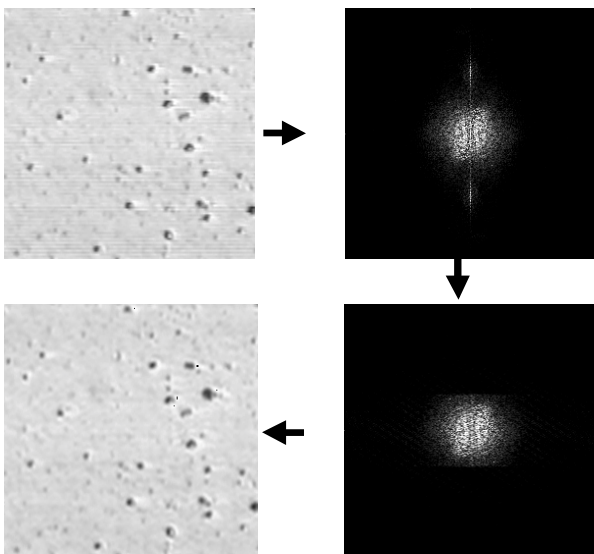
Based on OPTIMAS<sup>®</sup> we created a sophisticated macro program. Through several steps the shot is modified to enable a satisfying analysis.

First, motion of the particles is eliminated (Figure 7):

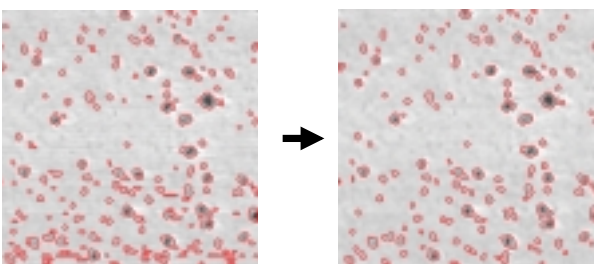


**Figure 7a.** Elimination of motion.

Then, stripes, caused by transformation of the analogous to the digital image are corrected by means of Fast Fourier Transformation (see also Figure 7 and Figure 8).

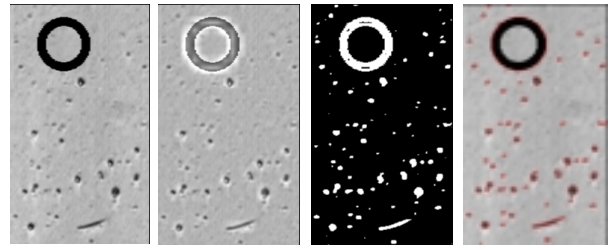


**Figure 7b.** Stripe correction.

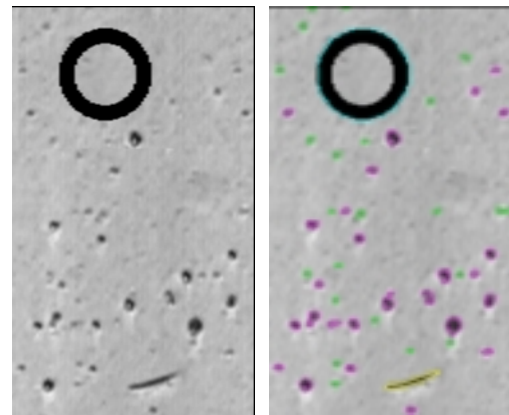


**Figure 8.** Difference in analysis of an uncorrected and a corrected image.

In the next steps illumination is corrected, the picture is binary coded leading to the identification of the individual objects (Figure 9). The objects are classified into fibers, air bubbles, transparent, and non-transparent particles (Figure 10).

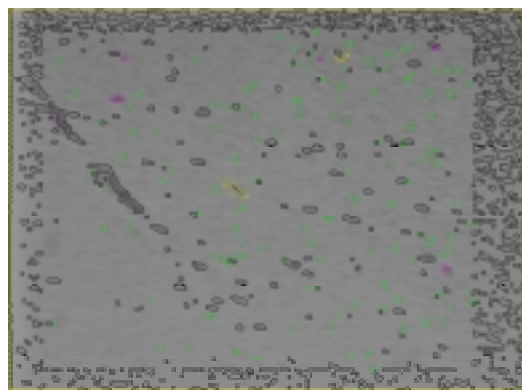


**Figure 9.** Identification of objects.



**Figure 10.** Classification.

During the period of a trial lasting several days, we checked the identification of deposits, which were built over night by almost stopping the flow through the cell. By comparison of several images, which are recorded and analyzed right before, the deposits are identified and excluded from analysis (Figure 11).



**Figure 11.** Identification of deposits (black marked).

Storing each image would soon lead to a “overcrowded” hard disc of the server. Therefore, we decided to export the results to a tiny text file. Images are stored too, when a set limit of particles is detected.

Common spread sheet programs can easily import the data allowing graphical evaluations.

**Conclusion**

We were successful in developing an online method for viscose quality control, by means of which we are able to analyze undiluted viscose. By our specially designed software we obtain number and size of impurities, there is a distinction between particle types, deposits inside the measuring device are detected, and our

system guarantees full functioning during continuous operation.

**Acknowledgement**

The author would like to thank the FEL group, Lenzing AG, and Ulrich Hirn, IPZ, TU Graz, for the good cooperation.

# CONTRIBUTIONS TO THE FLUID MECHANICS OF VISCOSE SPINNING

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The viscose wet spinning process is an important industrial process with highly complex physical and chemical interactions. Both media involved (spinning solution and spin bath) are fluids. Therefore, fluid mechanics play an important role and are a key science for a better understanding and further process development.

A new scientific approach, which combines the chemical and fluid mechanical aspects of the viscose wet spinning process as well as theoretical and numerical methods of fluid mechanics, is presented: a theoretical model for single filament spinning considering the chemical neutralization reaction, which is of central process importance, is proposed. With this approach it is possible to successfully predict the flow field, concentration profiles of sulfuric acid and sodium hydroxide in the bath and in the filament as well as the reaction front in the filament.

A simulation model of filament bundles allows for the comparison and optimization of

different spinneret designs by variation of the number, distribution and orientation of the holes on a spinneret surface with regard to hydrodynamic forces on the filaments and the gradient of sulfuric acid concentration.

Finally, a CFD approach is applied for computing the flow and concentration fields of sulfuric acid in an industrial filament production unit, in which hundreds of thousands of filaments are produced simultaneously.

It is demonstrated that the proposed computer simulation model is an excellent tool for spinning process optimization, improvement of fiber quality and development of new spinneret designs leading to a better understanding of the complex mechanisms in viscose fiber spinning.

**Keywords:** viscose wet spinning process, fluid mechanics, forces on filaments, conjugate mass transfer, neutralization reaction

## Introduction

Annually, two million tons of man-made fibers are produced by the viscose wet spinning process worldwide. In this important industrial process a number of highly complex physical and chemical interactions, such as visco-elastic material behavior, solidification of the filaments in a highly swollen state, complex chemical reactions, interaction with hydrodynamic forces and associated filament deformations, take place. During the production process spinning faults leading to poor product quality can occur. The main reasons for faults include the occurrence of splinters and fused fibers due to insufficient regeneration because of an uneven distribution of

the sulfuric acid concentration and the breaking of individual filaments by hydrodynamic shearing forces in the spin bath.

Although the importance of a sufficient supply of sulfuric acid, a uniform distribution of the acid concentration across the spinneret and a well-controlled flow of the spinning bath is well known from an empirical perspective, the scientific basis for a description and modeling of such phenomena is still rather poor.

In this paper a rigorous scientific approach, which applies theoretical and numerical methods of fluid mechanics, is followed to investigate the flow field as well as associated hydrodynamic forces on the filaments and the transport of sulfuric acid into the filaments.



In contrast to established models for wet spinning processes in the literature [11, 12] this new approach considers the chemical neutralization reaction, which is of central importance in the viscose wet spinning process.

### A new model for single filaments

The elementary problem of single filament spinning is discussed. The spinning solution, a non-Newtonian solution of cellulose xanthate in caustic soda is extruded through a spinneret into an acidic precipitation bath forming solidifying filaments of regenerated cellulose (Figure 1, an explanation of symbols is given in Table 1 in the appendix). Coagulation of the viscose and diffusion of the acid into the filament by neutralization of the alkali and decomposition of the xanthate are the main reactions during spinning.

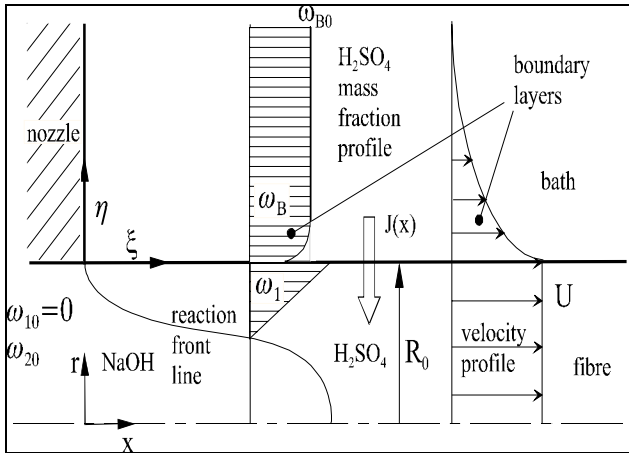


Figure 1. Model for a single filament.

The filament is pulled with velocity  $U$  through the bath by the godet. Because of the movement of the filament and due to viscous forces a flow is induced in the spin bath, as indicated in Figure 1. Axial flow velocities are high in the vicinity of the filament ( $u = U$  at the surface of the filament) and decay with increasing radial distance to the fiber.

This flow field is a typical boundary layer flow and it is computed by solving the steady, laminar and incompressible boundary layer equations [8]

$$\frac{\partial u}{\partial x} + \frac{1}{r} \frac{\partial(rv)}{\partial r} = 0 \quad (1)$$

and

$$\left(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial r}\right) = \frac{\nu}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r}\right) \quad (2)$$

for the axial and radial velocity components  $u$  and  $v$  of the velocity vector

$$\vec{u} = \begin{pmatrix} u \\ v \end{pmatrix} \quad (3)$$

in the spin bath. The velocity boundary layer is defined as the region, where the spin bath moves with an axial velocity component of at least 1% of the filament velocity,

$$u > 0.01U. \quad (4)$$

Axial velocity profiles  $u(r)$  for different distances  $x$  to the nozzle (spinneret) are given in Figure 2.

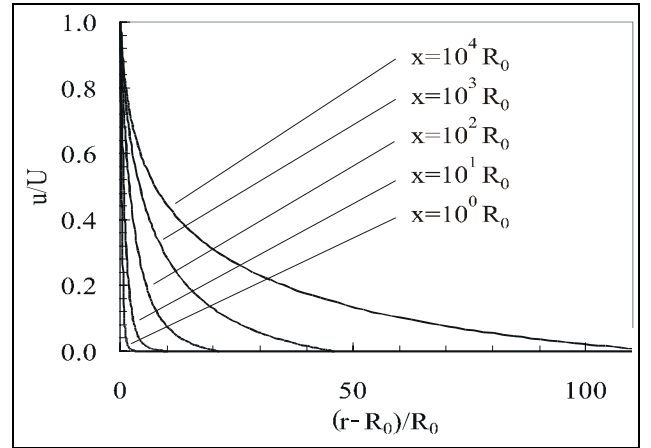


Figure 2. Axial velocity profiles.

As clearly visible in Figure 2 and displayed in Figure 9, the velocity boundary layer grows in thickness with increasing filament length  $x$ . Therefore the filament pulls an increasing amount of spin bath with it, the longer it gets.

To accelerate this increasing mass of spin bath in the boundary layer a force is necessary. This force is the reaction force to the braking drag force on the fiber, which is given by the integral of the surface shear stress,

$$F_D = \int 2\pi R_0 \tau_w dx, \quad (5)$$

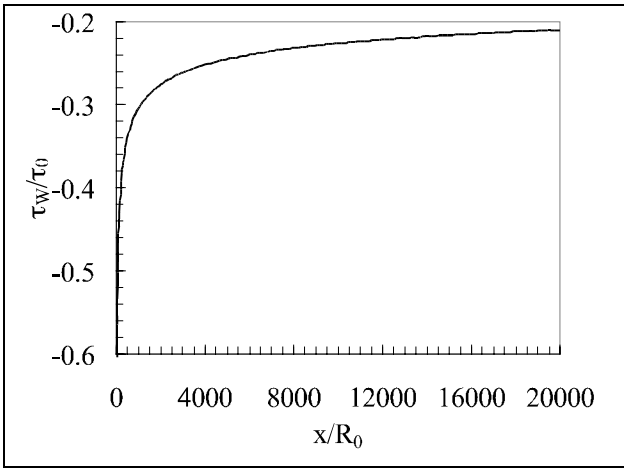
where this shear stress (on the surface of the filament) is given by

$$\tau_w = \rho \nu \frac{\partial u}{\partial r}. \quad (6)$$

The surface shear stress is therefore determined by the flow field and its distribution along the filament length is given in Figure 3, where

$$\tau_0 = \rho v \frac{U}{R_0}. \quad (7)$$

The surface shear stress is negative because it is directed against the filament motion. It can be clearly seen, that the surface shear stress is maximum at the tip of the filament (at the spinneret hole), where the filament is most sensitive because solidification has just started.



**Figure 3.** Filament surface shear stress.

Due to concentration gradients sulfuric acid is transported into the filament diffusively and reacts with the sodium hydroxide in the filament.

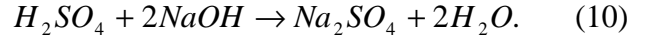
The mass flux density  $J(x)$ , which is the mass of sulfuric acid transported into the filament per unit area over its surface, is on the one hand determined by the flow field and diffusion in the spin bath, and on the other hand by diffusion in the filament. Therefore, this is a so called 'conjugate mass transfer problem'. Mathematically this can be described by diffusion/convection equations [1]

$$\left(u \frac{\partial \omega_B}{\partial x} + v \frac{\partial \omega_B}{\partial r}\right) = D_B \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \omega_B}{\partial r}\right) + \frac{\partial^2 \omega_B}{\partial x^2}\right) \quad (8)$$

for the mass fraction of  $H_2SO_4$  in the spin bath  $\omega_B$  and

$$U \frac{\partial \omega_1}{\partial x} = D_1 \left(\frac{1}{r} \frac{\partial \omega_1}{\partial r} + \frac{\partial^2 \omega_1}{\partial x^2}\right) + \Gamma_1 \quad (9)$$

for the mass fraction of  $H_2SO_4$  in the filament  $\omega_1$ , where  $\Gamma_1$  considers the consumption of sulfuric acid due to the neutralization reaction:



An equation similar to (9) is solved for the mass fraction of sodium hydroxide in the filament  $\omega_2$ . The neutralization reaction (10) is considered transport controlled.

With this approach, the mass fractions of sulfuric acid and sodium hydroxide in the filament can be calculated as given in Figures 4 and 5. The reaction front, as it emerges through the moving filament, is given in Figure 6.

The mass flow density of sulfuric acid  $J(x)$  through the surface of the filament is given in Figure 7, where

$$J_0 = \omega_{B0} \rho U. \quad (11)$$

The maximum mass transfer occurs at the tip of the filament directly at the spinneret hole, where the concentration gradient is maximum. The corresponding mass fraction of sulfuric acid in the bath at the surface of the filament is given in Figure 8. Its minimum value is at the tip of the fiber and increases monotonically with filament length.

This again illustrates, that the critical point of the viscose wet spinning process is at the tip of the filament directly at the spinneret hole, where the surface shear stress and  $H_2SO_4$  mass transfer are maximum, the sulfuric acid consumption is minimum and only a thin shell at the outside of the filament is solidified.

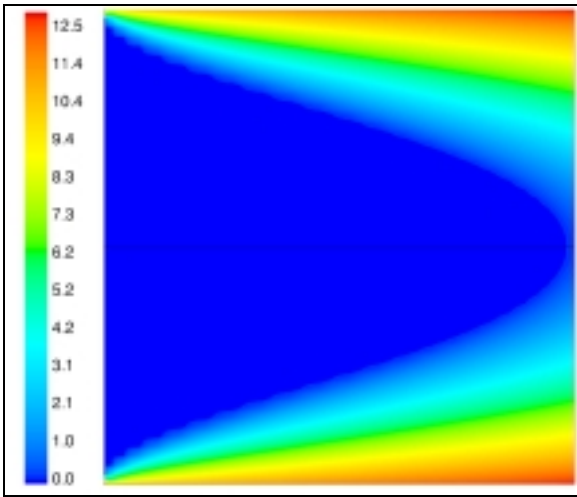
Because of the mass transfer of sulfuric acid into the filament, a concentration boundary layer (indicated in Figure 1), which is the region where

$$\omega_B < 0.99\omega_{B0}, \quad (12)$$

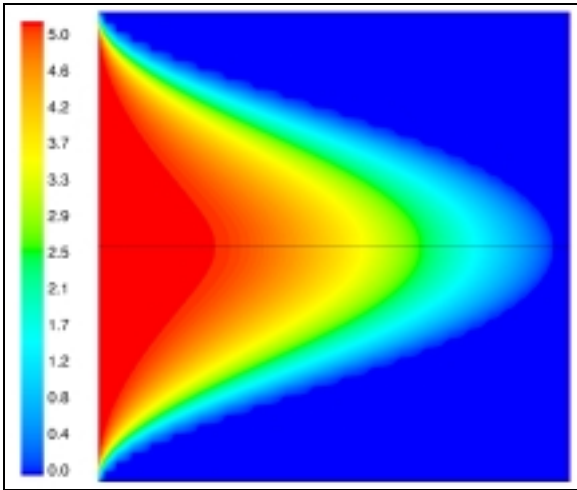
develops around the filament. Due to the high Schmidt number in the bath

$$Sc = \frac{v}{D_B} \sim 250 \quad (13)$$

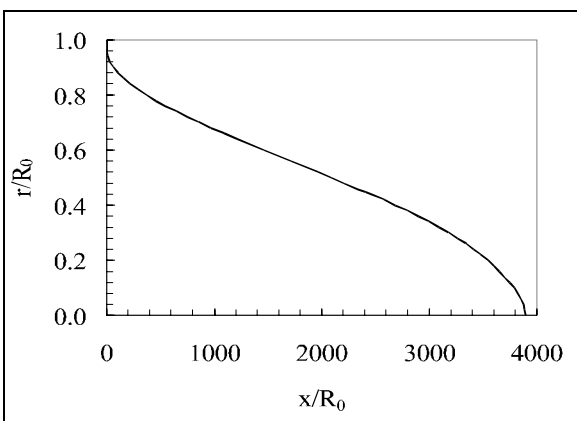
this concentration boundary layer is of much smaller scale than the velocity boundary layer (Figure 9).



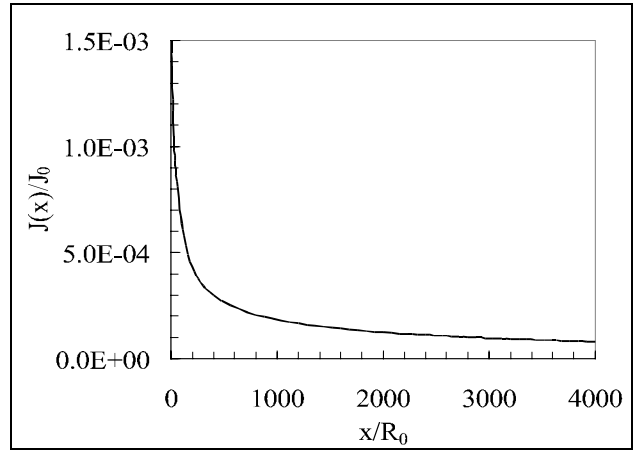
**Figure 4.** Contours of  $\text{H}_2\text{SO}_4$  mass fraction [%] in the range  $0 < x < 4000 R_0$ .



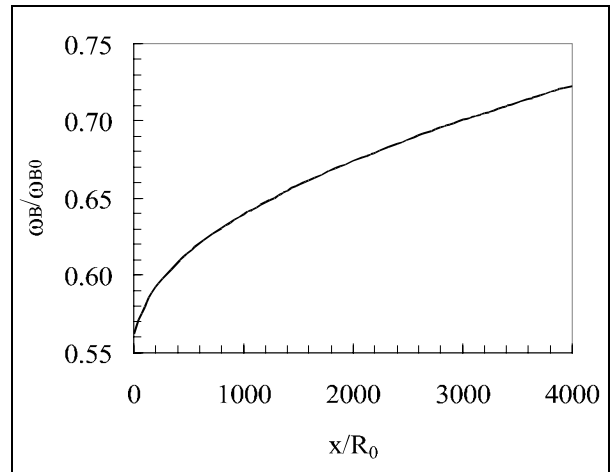
**Figure 5.** Contours of  $\text{NaOH}$  mass fraction [%] in the range  $0 < x < 4000 R_0$ .



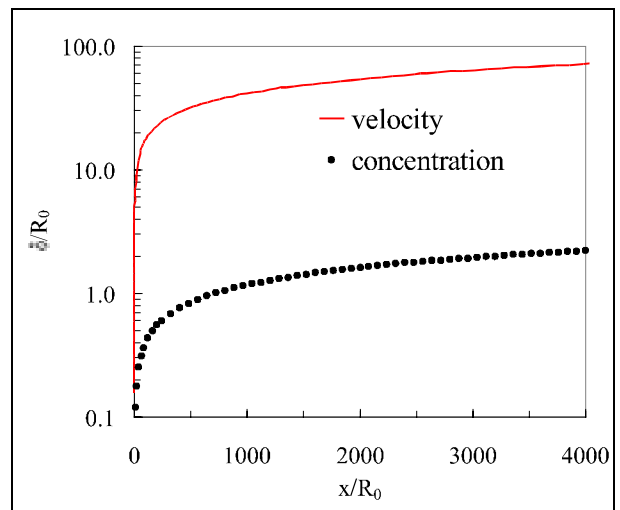
**Figure 6.** Reaction front in the filament.



**Figure 7.** Mass flow density of  $\text{H}_2\text{SO}_4$  at the filament surface.

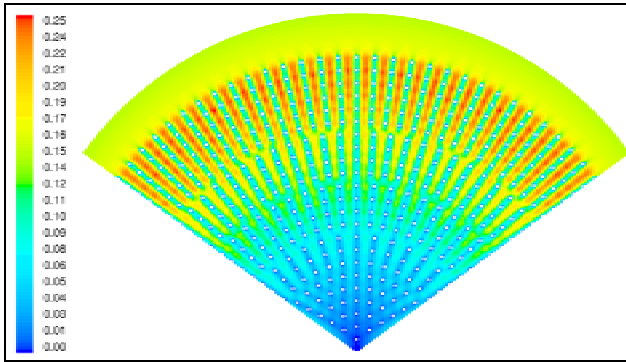


**Figure 8.** Mass fraction of  $\text{H}_2\text{SO}_4$  in the bath at the filament surface.

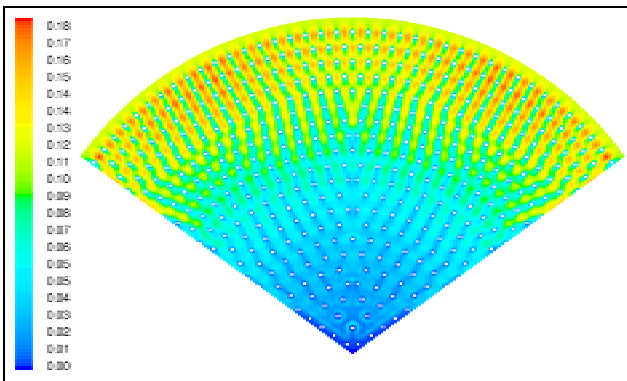


**Figure 9.** Thickness of boundary layers.

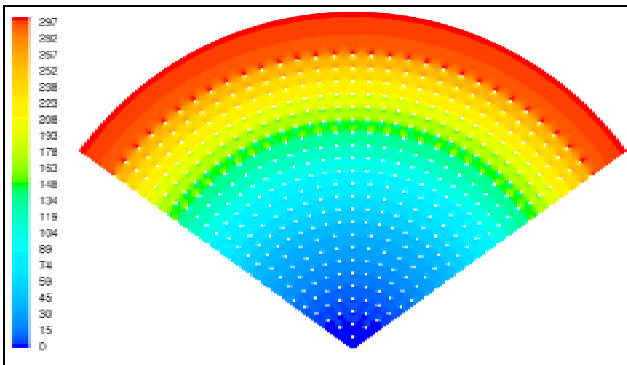
For an exact and efficient resolution of this small scale layer a combined theoretical and numerical methods, in particular the local non-similarity method [2, 9], is applied.



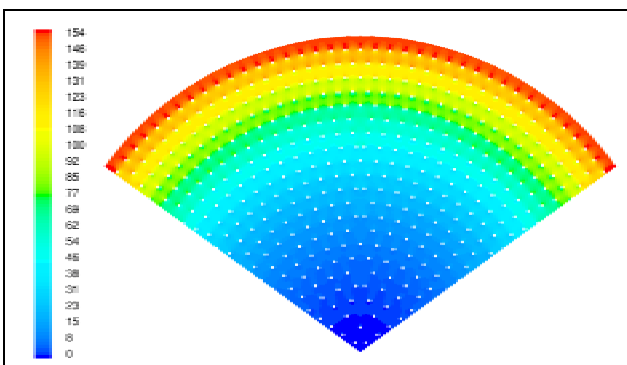
**Figure 10.** Configuration 1: in-plane velocity distribution [m/s].



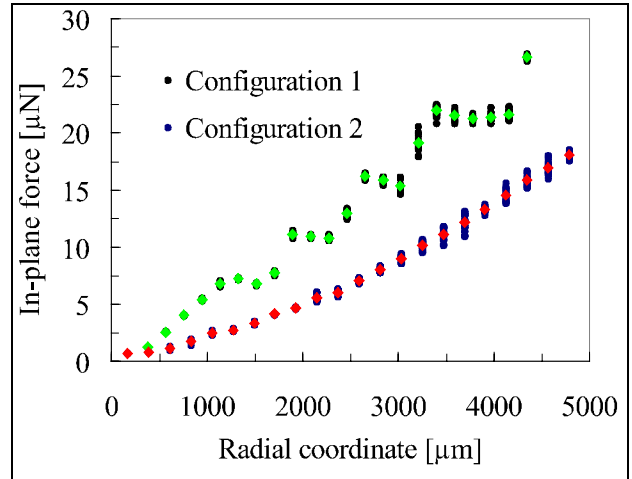
**Figure 11.** Configuration 2: in-plane velocity distribution [m/s].



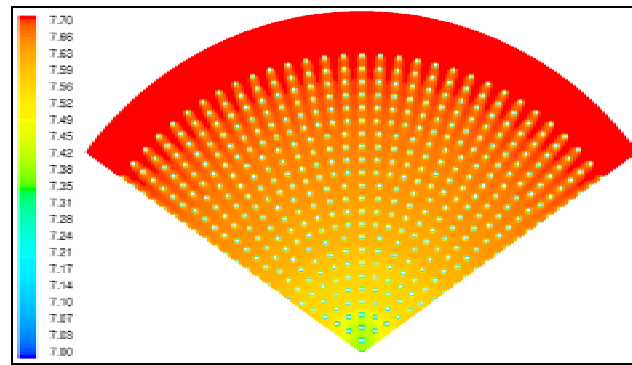
**Figure 12.** Configuration 1: pressure distribution [Pa].



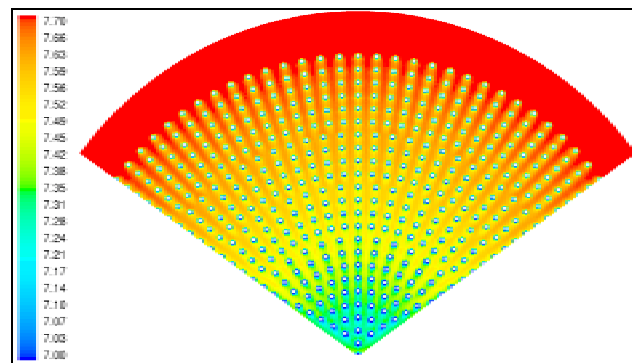
**Figure 13.** Configuration 2: pressure distribution [Pa].



**Figure 14.** In-plane forces on filaments (dots: individual values, diamonds: averaged values).



**Figure 15.** Configuration 1: mass fraction of  $\text{H}_2\text{SO}_4$  [%] close to the spinneret.



**Figure 16.** Configuration 1: mass fraction of  $\text{H}_2\text{SO}_4$  [%] in some distance to the spinneret.

The equations in the bath phase and in the filament phase are coupled at the phase boundary by relations for the mass flow density and chemical activity for sulfuric acid. Activity coefficients of  $\text{H}_2\text{SO}_4$  have been taken from [6]. The value of sulfuric acid concentration at the tip of the filament as given in Figure 8 is determined

by the analysis of a mass transfer contact problem as described in [3].

In practice, the radius of the filament is not constant along its length because of filament elongation due to the take-up force and because of water release due to the chemical reaction. An extension to a non-constant filament diameter based on a perturbation approach is given in [5]. A discussion of the proposed approach in full detail can be found in [4].

### Analysis of Cup Designs

Spinneret designs used in industrial wet spinning machines consist of a multitude of spinneret holes, either directly punched on a full spinneret plate in a certain manner or designed by assembling a group of smaller units ('cups' or 'eyes') to form cluster spinnerets. These cups are usually designed by various heuristic grouping strategies, which are usually evaluated experimentally.

Here, a rigorous scientific approach is proposed to evaluate different cup designs: the flow pattern as well as pressure and concentration fields in the spin bath as induced by different cup designs are computed and evaluated with regard to hydrodynamic forces on the filaments and sulfuric acid concentrations on the surface of the filaments.

Figures 10 and 11 show in-plane velocity distributions for two different configurations. The pressure distribution in the spin bath is given in Figures 12 and 13. The pressure drop from outside of the filament bundles to the center is higher for configuration 1. A comparison of hydrodynamic forces on the filaments is given in Figure 14, where the radial coordinate is the distance of a filament to the center of the cup. In this flow regime viscous and pressure forces are approximately of the same order of magnitude.

The mass fraction of  $\text{H}_2\text{SO}_4$  in the spin bath is displayed in Figures 15 and 16 for different distances to the spinneret. A more detailed discussion of the analysis of cup designs can be found in [7].

### Industrial Filament Production Unit

As an example of an investigation of an industrial filament production unit the analysis of the flow and concentration fields in a spin tube is

presented here. The purpose of this analysis is to clarify if spinning faults are caused by an excessively low concentration of sulfuric acid.

The flow of the spin bath is primarily driven by the moving filaments (through the action of viscous forces) and by a pump. The streamlines in the spin tube colored by  $\text{H}_2\text{SO}_4$  mass fraction are shown in Figure 17. The mass fraction of sulfuric acid on vertical plane in the spin tube is given in Figure 18.

Due to the enormous geometrical complexity (hundreds of thousands of filaments) this simulation approach relies on modeling the effects of small-scale structures on large scales (each of the cylinders in Figure 17 represents the filaments emerging from a cup).

### Summary and Conclusions

In this paper the viscose wet spinning process has been investigated with an approach that combines the chemical and fluid mechanical aspects.

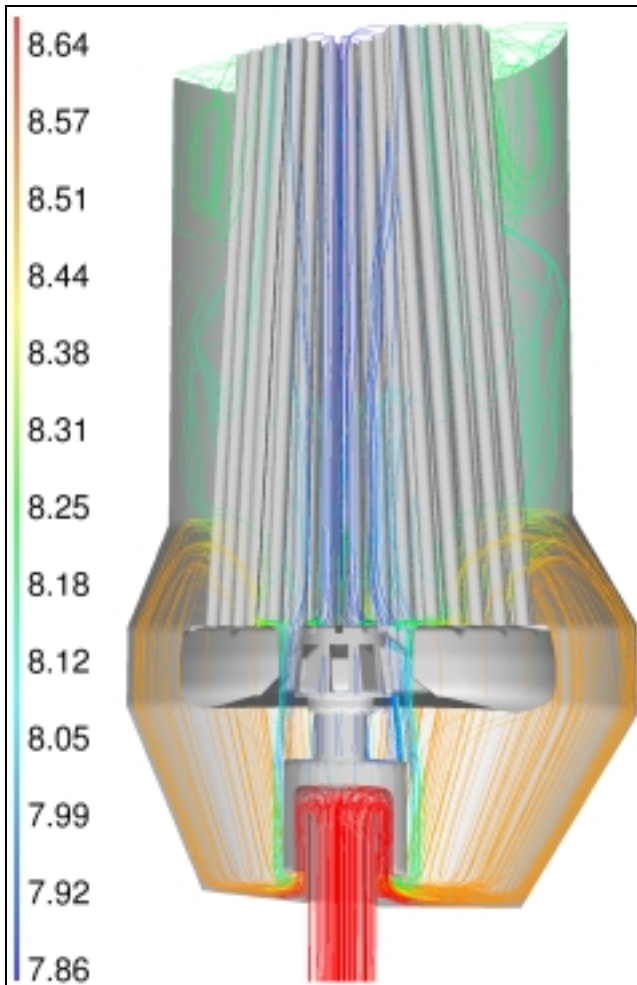
The flow field, hydrodynamic forces on the filaments, the neutralization reaction front in the filament and the concentrations of sodium hydroxide and sulfuric acid in the filament and in the spin bath have been calculated.

It has been demonstrated that with this method spinneret configurations can be designed and evaluated with respect to hydrodynamic forces on the filaments and the sulfuric acid concentration gradient in the spin bath.

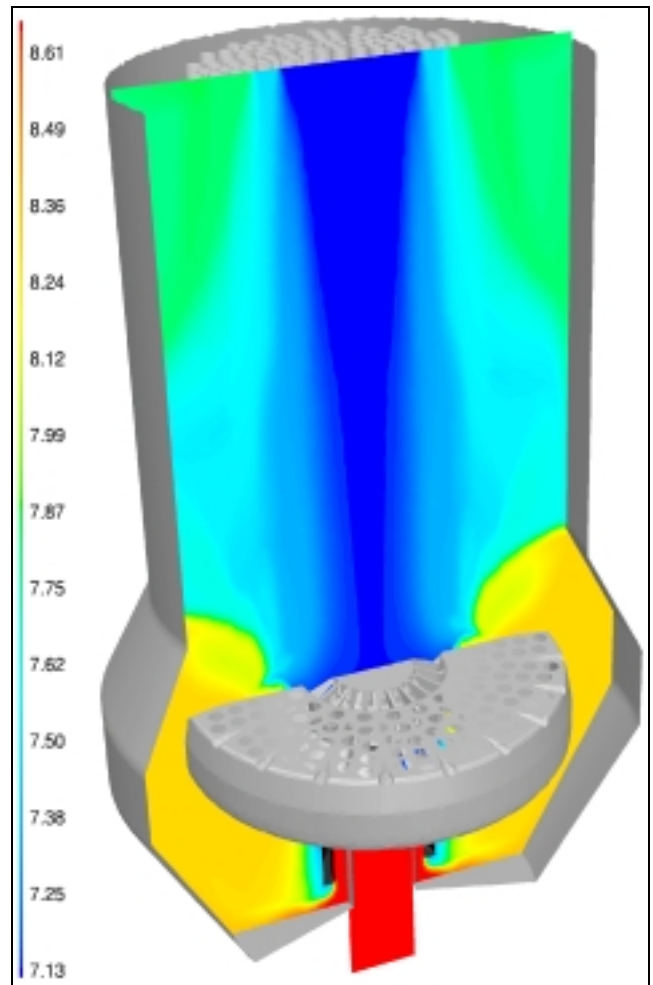
Furthermore the effect of parameter variations (such as filament radius, spinning speed, spin bath  $\text{H}_2\text{SO}_4$  concentration, etc.) and their influence on the spinning process can be studied.

Although the presented investigations represent some substantial progress in the understanding of this complex process there remains a lot of work to be done. Possible further research on the viscose wet spinning process may deal with e.g. the modeling of more complex chemical reactions, solidification effects, temperature differences, visco-elastic effects, multi-phase flow.

An especially important fact seems to be the efficient description of hydrodynamic forces on the filaments and associated deformation (fluid-structure interaction), because these have proven to be central issues for the spinning process.



**Figure 17.** Streamlines in the spin tube coloured by  $\text{H}_2\text{SO}_4$  mass fraction [%].



**Figure 18.** Mass fraction of  $\text{H}_2\text{SO}_4$  [%] in the spin tube.

## Acknowledgements

I am grateful to Lenzing AG, who has encouraged the successful submission of this research to the Paul-Schlack-Award competition in 2002.

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## Appendix

Symbol	Description
$D_B$	diffusion coefficient of $H_2SO_4$ in the bath
$D_1$	diffusion coefficient of $H_2SO_4$ in the filament
$J$	surface mass flow density of $H_2SO_4$
$R_0$	filament radius
$U$	filament velocity
$r$	radial coordiante
$u$	axial bath velocity component
$v$	radial bath velocity component
$x$	axial coordinate
$\Gamma_1$	reaction source term
$\rho$	spin bath density
$\nu$	spin bath kinematic viscosity
$\tau_w$	filament surface shear stress
$\omega_1$	mass fraction of $H_2SO_4$ in the filament
$\omega_2$	mass fraction of NaOH in the filament
$\omega_B$	mass fraction of $H_2SO_4$ in the bath
$\omega_{10}$	$H_2SO_4$ mass fraction of fresh spin solution = 0
$\omega_{20}$	NaOH mass fraction of fresh spin solution
$\omega_{B0}$	$H_2SO_4$ mass fraction of fresh spin bath

**Table 1.** Nomenclature.

## HIGH SPEED SPINNING OF VISCOSE FILAMENT YARNS

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ENKA invested in the technology of high speed spinning to be prepared for the various developments in the textile market.

The continuous spinning process according the ENKA CHEV-technology can now be operated at 500 m/min spinning speed. At this speed, the production stability and the product properties are at an optimal level. Especially the level and the constancy of all important yarn properties, such as dye uptake

and shrinkage, are excellent. Also at manifolded spinning speed, the special ENKA continuous spinning process shows the advantages in product properties in comparison to the Nelson-type technologies. Further increase in spinning speed is limited by mass-transfer in the yarn forming step and the washing units. Technically, a spinning above 1000 m/min is possible, but ENKA sees no economical benefit at this high speed.

### Introduction

The viscose technology is the origin of the man-made fiber industry. The current basic technologies were developed in the years 1950 to 1960. These technologies are known as

- *Spool process*
- *Pot – or centrifuge process*
- *Continuous process.*

For ENKA, it was the target to clarify the potential of all of these technologies. The discontinuous processes are highly optimized. At our plant Elsterberg, the most modern spool process was built in 1991 to 1993, by utilization of all optimization potential of the individual process stages.

This paper will show the options and possibilities of the continuous technology. Target of the 5-year development was to improve the productivity by manifolded the process speed.

### Current situation : viscose filament

The development of the high-speed spinning process started at ENKA in the early 90s, a time of high demand for viscose filament yarns. A first phase of restructuring was finished,

materials with natural origin were en vogue especially in Italy.

In the years 1998 to 2000, we faced in Europe a trend towards “TECHNO” materials, based on polyamide and polyester. This trend leads to a further decrease of the viscose filament capacities worldwide. In 2002, some recession and a weak demand in the US hit the total textile industry. This situation already influenced the top textile industry and will surely have impact on the yarn industry.

As a consequence, in the past 2 years, the viscose filament capacity worldwide decreased by more than 30%. If the temporary weakness will last longer, a further capacity reduction will take place.

### Quality requirements for viscose filament yarns

The textile applications for viscose filament yarns have remained basically unchanged over the past decades. In the apparel segments, viscose filament yarns are used for crepe fabrics, knitwear, embroideries and yarn blends together with wool or synthetics.

For garment lining fabrics, viscose filament yarns are still the most favorable materials to get the right fabric properties.



Dependent on the fashion cycles, these various segments are characterized by strong fluctuations in demand.

A successful yarn process for these markets has to be designed for high flexibility to cover all these applications. The titer range has to cover all segments; the technical performance of the yarns has to be suitable for these various textile-processing steps. For ENKA, which serves all these textile segments, the basic yarn properties

- *Constant dye uptake,*
  - *Consistency in all physical properties,*
  - *Excellent mechanical processing properties*
- have to be the premises for the high-speed spinning process. In the current textile industry, where time to market is the ultimate requirement, product deviations influencing the processability or fabric characteristics are not tolerated.

### Technical requirements for the high-speed spinning process

Based on the market demands, the technical requirements can be defined.

*Constant dyestuff uptake* is achieved by constant skin-core relation and porosity. This means constant process parameters, such as temperatures, concentrations, and residence time throughout all process steps.

*Excellent mechanical processability* requires a low number of contacts of yarn and machine parts, high quality of the surface of yarn guides, godets with a controlled drive and a safeguarded protection of the individual filaments in all process steps.

*Basic tenacity and elongation* is tuned by the spin bath and viscose solution parameters.

### Comparison of existing technologies

The known processes can be divided into four basic technologies. Spool and pot-processes are both discontinuous types. For all the various steps (spinning, washing, drying and winding) the optimal processing speed and parameters can be chosen. The disadvantage is the high labor intensity and high processing times. Within these two discontinuous technologies, the spool process covers a titer range from 67 dtex to 660 dtex at top quality; the pot process

is more restricted to the heavy deniers. ENKA therefore divested the production plants based on pot spinning and invested in spool technology in Elsterberg.

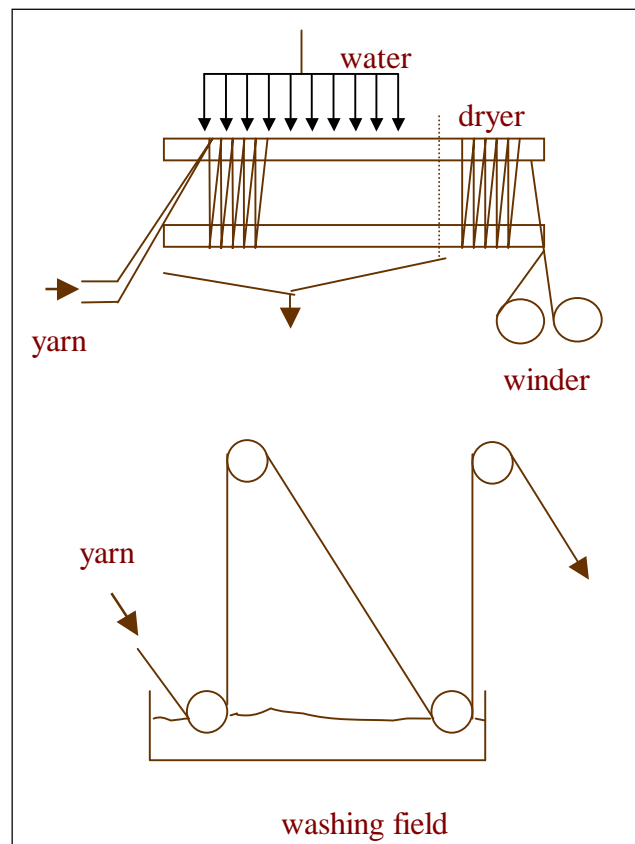


Figure 1. Nelson and ENKA CHEV principle.

The Nelson and the ENKA CHEV technology are both continuous processes with short production time (Figure 1). The compact Nelson process realizes the post-coagulation step and the yarn washing with low space requirements. This results in comparatively low investment costs. This benefit in investment leads to a weakness in parameter constancy during these process steps. Result is the broad variance in physical yarn properties and dyeing characteristics.

The technical more sophisticated ENKA CHEV process has a parallel yarn treatment. The different washing steps are fully separated and can be operated at optimal conditions. As a result, the quality of the CHEV yarns is fully comparable to the spool spun yarns.

## Development of high-speed spinning viscose filament

ENKA started the development of high speed spinning to reduce the specific investment cost of the CHEV process, which were clear higher than for a Nelson process. The product portfolio had to cover the titer range from 40 dtex to 167 dtex at the established ENKA quality level. Especially the yarn shrinkage of max. 5 % was to be kept beyond this limit. The target spinning speed was defined as 500 m/min, which meant a factor of 3 to 5 in comparison to the established speed.

### Process principle for high-speed spinning

In a continuous spinning process, the yarn speed in every step has to be identical. The dimensions of each unit are determined by the necessary residence time. For a minimized investment and therefore the optimal economics, the target is to reduce these residence times as much as possible. An alternative to operate the process steps of a continuous spinning at different speeds was developed by Asahi. The high-speed yarn formation was followed by a low speed washing, where the yarn was folded on a sieve belt. ENKA did not follow this process strategy due to our demands in quality and process stability.

The mass transfer mainly determines the residence times of the processing steps. The time limiting mass transfer is of course different during coagulation, degradation of the xanthate, washing and drying.

The first step, the chemical reaction, is a fast neutralization of sulphuric acid and caustic. The reaction rate depends only on the acid diffusion to the reaction zone. The washing process is only controlled by diffusion. The limiting mass transfer coefficients of e.g. sodium sulphate in cellulose and in the laminar film are constant. Drying is also a diffusion process where heat transfer and the diffusion coefficient of water in cellulose are the determining items. Common for these types of diffusion processes are the limited possibilities for acceleration of mass transfer.

## Yarn Formation

The principle of yarn formation had to be developed according a totally new approach. The residence time for fiber formation is constant due to diffusion of acid into the filaments. A stagnant spin bath similar to spool spinning allows only a spinning speed of 150-200 m/min. At higher speed, the friction of bath to fiber is too high, so that the yarn will break. With a spinning tube according the CHEV technology, an increase of speed can be achieved. Here the limits are the risk of turbulent flow of spin bath in the tube resulting in a kind of intermingling of the filaments. The only way, in our experience, to spin at 500 m/min or faster is the use of a free falling spin bath (Figures 2 and 3).

### Washing Process

The washing section gives the opportunity to increase the mass transfer to a high extent. The diffusion barriers of the total filament bundle can be increased by opening this bundle. The target in the washing section is to limit the film diffusion at the filament.

### Drying Process

Contact dryers can reach high heat transfer rates. Other drying technologies, such as convection or microwave, do not have the efficiency. Here, component suppliers can offer an optimal technology.

### Pilot plant

A pilot plant with a 100 t/y capacity, engineered by ENKA, was operated for 2 years. In this pilot phase, all important components were tested, various yarn types were produced and processed according all typical viscose filament applications. The yarn titers 40 dtex up to 167 dtex could be spun at 500 m/min. The higher deniers required a reduction in spinning speed due to the mass transfer limitations. For these yarn types, the typical ENKA product properties were reached. The process stability at high speed is much more demanding. Yarn tension control throughout the total process steps is a must, requiring a sophisticated and also robust control system of the godet drives.

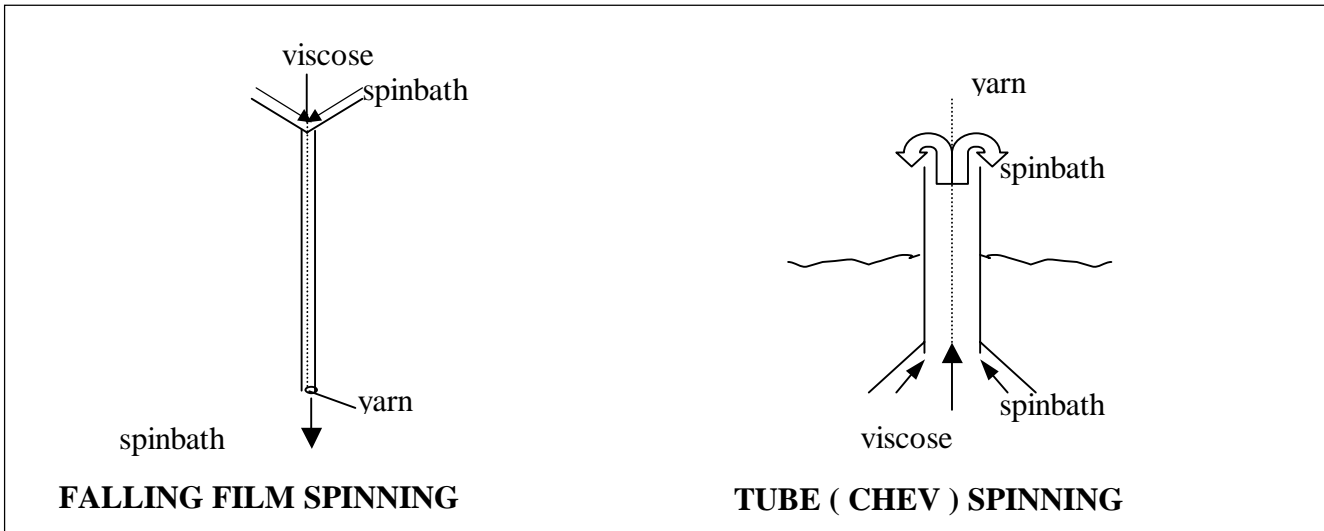


Figure 2. Comparison of spinning.

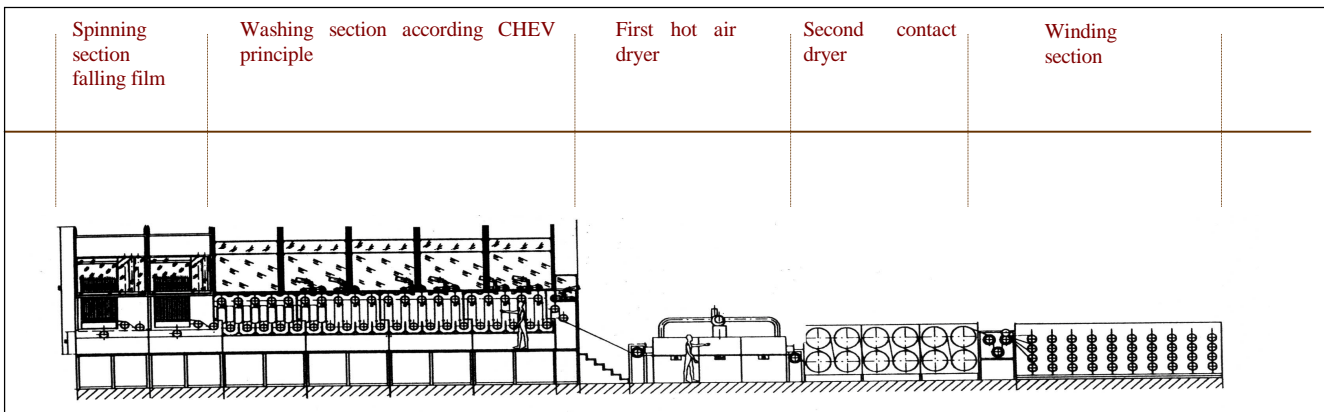


Figure 3. Process scheme.

### Limits of High Speed Spinning

The major technical limit is mass transfer within the bulk phase of the individual filaments and the mass transfer restrictions of film diffusion. An increase of spinning speed can be achieved by a proportional increase of

- *Falling film length*
- *Number of washing elements*
- *Number of drying rolls*

with increasing speed, the process stability will become the determining limit. Yarn breaks are more difficult to control, the probability to restart the total machine after minor problems increases. According ENKA's experience, the achieved 500 m/min spinning speed is the current optimum between efficiency and process stability.

The increase in spinning speed by factor 4 shows the potential of the viscose technology, which has already a history of about 100 years. By this development, the specific investment costs for a continuous filament production based on ENKA's CHEV technology is favorable compared to the Nelson technology. By implementing the advanced process, the investment costs would be economically attractive. ENKA is therefore prepared for all possible market situations.

# NEW WET OPENER – SYSTEM BLOW DRYER BY LENZING TECHNIK

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## Introduction

Being an innovative company, Lenzing Technik (LT) has set itself the task of constantly observing the needs and trends in the market place to be able to analyze solutions to problems and modifications in good time, and to be able to present these to individual and potential producers.

This approach led to the development of the new „Wet Opener – System Blow Dryer“ from Lenzing Technik (Figure 1). This paper will inform about this development and present details of the status of our development work.

The goal was a device with simplified fiber opening, while maintaining the gentle treatment of the wet fiber with an improved formation of

an opened fiber mat on the subsequent dryer, which can either be a drum dryer or a belt dryer. Moreover the following goals have to be fulfilled:

- Reduction of the investment costs compared to conventional solutions
- Reduction of the well-known high maintenance and repair costs
- Elimination of possible fiber contaminations (lubricants, fats)
- Capacity increase potential with a replacement investment

At the very outset I would like to state that we have reached these goals and are thus able to offer a successful technical solution.

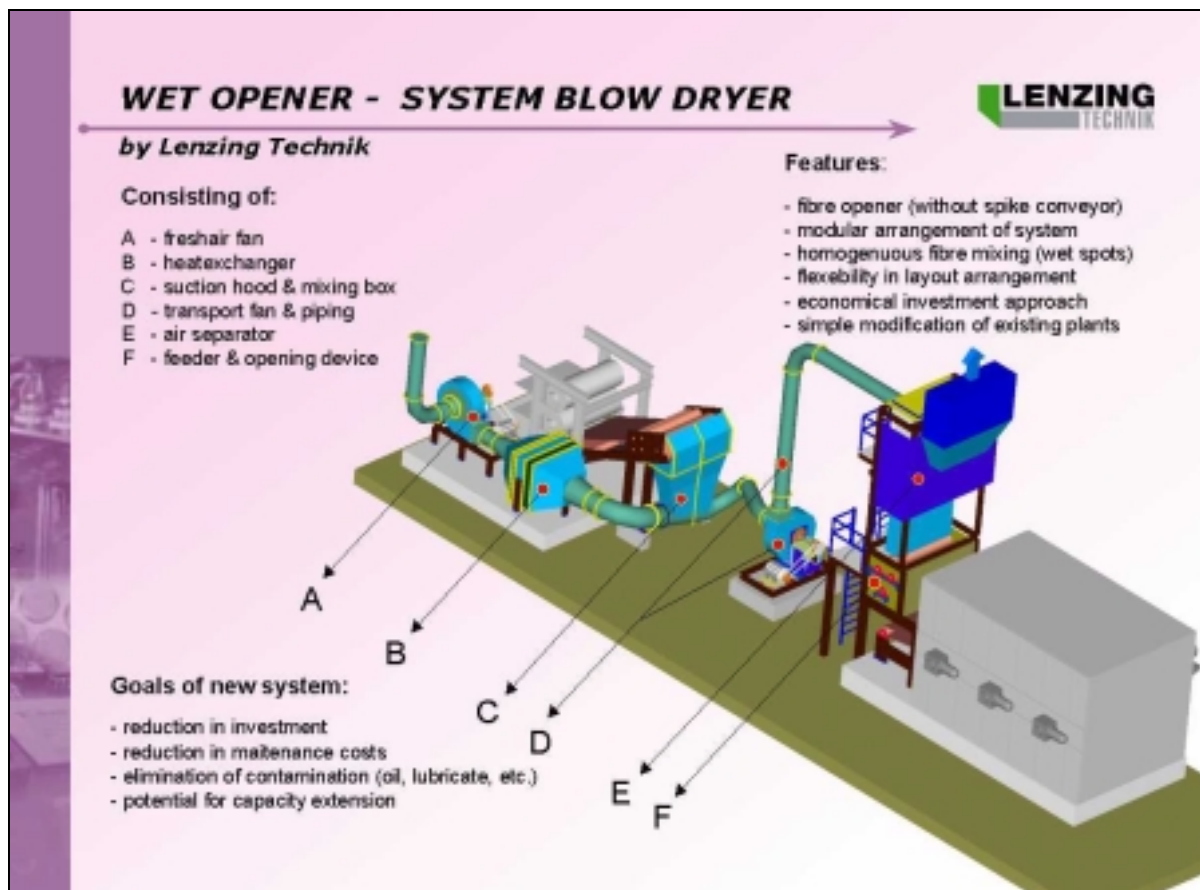


Figure 1. Schematic of the wet opener- system blow dryer.

## Description and mode of operation

The „Wet Opener – System Blow Dryer“ is a new and important device to open fibers after the aftertreatment. The fiber is still wet here with a moisture content of around 105 % to 110 % and in a state in which fiber damage can easily occur by mechanical overstressing, since the fiber is difficult to open depending on the type and the treatment.

In this new opener, the fiber is treated very gently with only one mechanical opening part, the opening device. The essential opening effect is performed by the combination of the blown air transportation and the opening device. It is well-known that the force requirement for opening of a wet fiber will decrease to the extent that the fiber loses the moisture, and the risk of fiber damage by mechanical loads decreases in the same course. The “Wet Opener – System Blow Dryer“ does justice to this realization.

The use of a blown air device here is definitely nothing new to the fiber industry. However, the use of this in the combination of a drying system with a wet opener is new.

The amount of blown air required for fiber transportation and drying is heated up via a heat exchanger and applied to the wet fiber in a so-called mixing chamber. This is then led via the transportation fan to the actual opening device via an air separator. The heat exchanger can either be heated with steam, gas or electricity. The transportation fan used has to have a special design for the task of transporting the damp fiber. In the air separator the transportation air is separated from the fiber and the fiber falls into a shaft where it is opened via the opening device comprising the feed rolls and the opening tambour.

A certain amount of moisture is correspondingly removed from the fiber as a result of transportation via the ventilating fan and the feed. This simplifies the subsequent opening of the fiber in the opening device quite considerably.

The spike conveyors used in conventional wet openers are no longer used here. The fiber opening is mostly equally as good, if not better, than compared with the plants used until now.

Another important advantage is an as a whole better opened fiber, mixed homogeneously

across the working width in the following dryer inlet. Well-known wet-spots are considerably reduced whereby the dryer performance is more efficiently made use of in terms of an increase in capacity.

As shown in Figure 2, the transition of moisture is carried out in a very short space of time. The turbulent air control and efficient mixture with the fiber leads to rapid evaporation of the liquid and in turn to drying of the fiber. This effect is utilized in the new „Wet Opener – System Blow Dryer“. Since the fiber can be admitted in the wet state without any danger with a very high temperature, a considerably high content of moisture can be evaporated at this stage in a highly economical manner. The very gentle opening of the fiber is done in addition in only one equipment. The following dryers, particularly in the exiting production lines, can thus have corresponding relief of their loads, which can be used for other efforts, such as capacity increase.

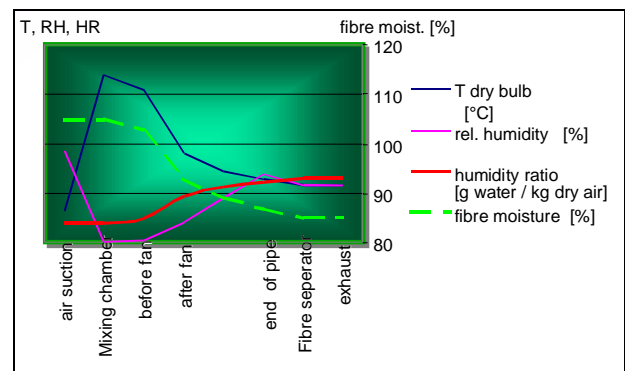


Figure 2. Temperature - fiber moisture diagram.

## Features

*Economic efficiency with regard to new and replacement investments.* The system offers the important advantage of very economic specific costs to increase the performance of existing production lines. The mechanically and technically mostly mature dryer lines undergo an increase in capacity as a result of an integrated „Wet Opener – System Blow Dryer“. Thus, for the first time a very attractive piece of equipment is available for production lines.

In the recent past in most cases only concepts were developed for new production lines „on grassroots basis“ with very long financing terms, thus making them difficult to finance.

Only a few producers have so far dared to modify existing production lines step-by-step, since specific engineering and planning know-how is required for this to reach the modification goal without any risks and to minimize the necessary production failures in the conversion phase. There were also hardly any systems available in the market, which would have been of use to producers. The SXS spinning technology from LT on a modular basis already took a major step forward only a short time ago. The innovation concept of LT is persistently continued with this new system. Producers can thus increase their fiber capacity simply and favorably without having to invest in a complete line.

*Low repair and maintenance costs.* The maintenance costs with this system have to be lower in view of the much simpler plant compared to conventional equipment:

- the number of mechanically moved parts is very low,
- the ventilating fans used and the piping is insignificantly low from the viewpoint of repairs
- the air separator is quite safe with regard to the risks for repairs.

It should be taken into consideration that all over the world in well-known production plants the section of wet opening and the spike conveyor have the highest specific repair costs. In addition the same area is responsible for most production failures. Until now this was money unwisely spent, causing a lower production availability.

Moreover, the aim is to considerably reduce the effort required for cleaning using the „Wet Opener – System Blow Dryer“ and to significantly improve the efficiency of cleaning. The accessibility of the equipment is simple and easy to accomplish.

*Opening device without the spike conveyor.* The new „Wet Feed & Blow Dryer“ is an opening device without a spike conveyor. Apart from the advantage already mentioned i.e. the reduction in repair and maintenance costs the system fulfils the task of treating the fiber with care via mechanical work. This will also benefit the fiber quality.

*Elimination of fiber contaminations.* The reduction of the moved and rotating mechanical parts in the system and the use of corresponding materials sufficiently does justice to the requirement to prevent any possible product contaminations (dirt, lubricants, etc.).

*Flexibility of plant layout.* The conception of the „Wet Opener – System Blow Dryer“ allows for a very flexible plant layout. The system design makes it possible to install it as you wish and thus save on building space. This advantage has economic consequences with regard to new respectively replacement investments.

*Modular System-Design and Plant Capacities.* The modular system design selected makes it possible to operate the different capacities of the plant in a very efficient manner. As a standard the common working widths of production lines are taken into consideration. As shown in Figure 3, we have already developed standardized calculation models so as to be able to calculate a customer-oriented capacity and layout very quickly.

## **Results to date**

Our experience to date has shown that the amounts of fiber produced were fully accepted by customers in the down stream processing. Thus apart from the examinations conducted in-house it is confirmed that the fiber quality produced is equally as good as that produced by conventional lines or was even improved upon with regard to individual values.

A reduction in the fiber moisture level by more than 20% is achieved with a prescribed amount of air and heating capacity. A given dryer can be extended in terms of its capacity by the equivalent of this amount of water content or the fiber drying can be performed in a gentler manner.

There is ample practical production experience with the wet opener part at our subsidiary in the USA and at the same time drying trials were successfully completed in production conditions.

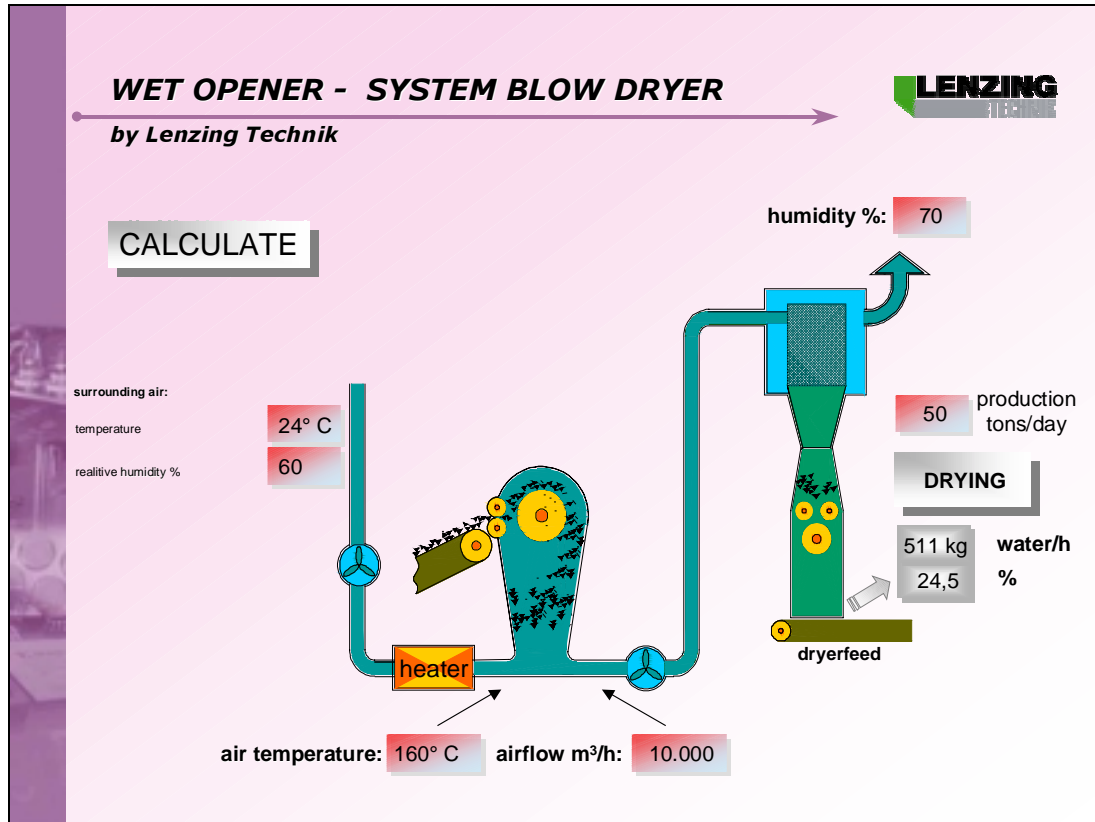


Figure 3. Cost calculations.

## Summary

The results we have received today acknowledge our concept and have encouraged us to march ahead with the marketing of our product.

The new „Wet Opener – System Blow Dryer“ from Lenzing Technik offers a definite alternative to the wet opening system used in numerous applications! There are already some attractive inquiries from interested parties and we are already negotiating with one of them.

## Acknowledgement

I would like to warmly thank my coworkers for their commitment and active support during the development phase of the new „Wet Opener – System Blow Dryer“ as well as for their help with this paper.

# QUANTITATIVE DETERMINATION OF CARBOXYL GROUPS IN CELLULOSE BY COMPLEXOMETRIC TITRATION

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Complexometric titration was used to determine the carboxyl group content of a series of oxidatively treated (selective and non-selective oxidation) nature cellulose fibers (cotton). The results were correlated with those obtained from the conventional methylene blue method; both methods show an excellent correlation. The progress of the cellulose fibers oxidation was monitored using viscosimetric determination of the molecular weight.

The content of carboxyl groups depends on the oxidation procedure and it is, in the case

of selectively oxidized fibers, twice as high as the content of carboxyls in raw fibers. The carboxyl group content for non-selectively oxidized fibers increased by approximately 180%, relative to untreated fibers.

The results of our investigation demonstrate clearly that complexometric titration is an excellent tool for monitoring the influence of chemical modifications on the carboxyl group content. This method is sensitive enough to determine small changes in the content of functional groups for chemically modified fibers.

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## Introduction

Cellulose fibers have a number of essential advantages expressed by costumer friendliness in comparison to synthetic textile polymers (PES, PA, PAC). Their main disadvantage is of technological nature, i.e., their finishing process is much more complex, and, therefore, environmentally aggravating. Although finishing processes have been used for several years, they are only partially understood, and better basic understanding is needed in order to gain some knowledge about their influence on fiber adsorption ability, hydrophilicity or the accessibility of active groups for the final fiber finishing as dyes or surfactants.

During the production and processing of cellulose materials, chemical (oxidation and hydrolysis) and structural modifications (degree of crystallinity and form of the unit cell) are applied in order to change the reactivity due to

an alteration in the number and allocation of functional groups and possible degradation. The processing of cellulose has an influence on the fibrillar structure, i.e., the cellulose structure is loosened, causing swelling of the polymer and increased accessibility of active groups on the fiber surface [1]. It is assumed that these modifications on the solid phase surfaces mainly change the interaction ability of the cellulose fibers with components at the liquid phase.

The fine structure of the cellulose fiber is already quite well understood, contrary to the reaction abilities of the fiber surfaces, which is correlated with the quantity and quality of the cellulose reactive accessible groups. It is extremely important to be able to determine the number of the accessible groups in order to judge the polymers' interaction ability, their ion exchange capacity and the progress of technological processes during the manufacturing of cellulose polymer materials.



Carboxyl groups in cellulose are able to act as sources of ion exchange capacities [1] and can be utilized to analyze the dissociation process in heterogeneous polymer systems, the polymers' reactivity and the accessibility of these groups. The ion-exchange properties of cellulose fibers can, therefore, be used to monitor the quantity of carboxyl end groups, which is a matter of special importance in order to control the progress of oxidation processes.

The amount of carboxyl groups present in the original material or created by oxidation can be determined by different techniques [2-6]. Methods involving both paper and column chromatographic techniques were evaluated as to their suitability for measuring the ion-exchange capacity of pulps and nitro pulps [2]. The spectroscopic methods and the method of exchange with the base of crystal violet in a non-aqueous medium have also been used [1,3]. A few methods including titration for determination of carbonyl groups and acidic groups in cellulose pulps are shown in the literature review [4-5].

In this paper, we present a new method for determining the amount of carboxyl groups in cellulose fibers based on the ion exchange reaction between calcium ions and carboxyl groups. This method is a modified Sobue-Okubo method [6], based on a determination of the remaining amount of calcium ions in the solution after ion exchange with cellulose fibers. Measurement of the decrease in cation concentration of the added calcium acetate solution was performed using a standard complexometric EDTA (ethylenediamine-tetraacetic acid) titration. The results of this method were compared with those obtained by the methylene blue method, where the methylene blue dye cations bound to the cellulose carboxyl groups were monitored spectrophotometrically.

Both methods, the methylene blue and the complexometric titration, are based on the ion exchange capacity of the cellulose. A

correlation of the results of both methods should make it possible to assess which one is more appropriate for the quantitative determination of carboxyl groups in cellulose.

## Experimental

Natural cellulose fibers (cotton) were modified in different ways in order to judge the ability of the new approach to analyze the behavior of celluloses after different chemical processes. They were chemically modified by oxidation in order to obtain different contents of carboxyl groups. The oxidation of cellulose causes an increase of both carboxyl and aldehyde groups depending on the oxidation and the reaction conditions [1].

Oxidation processes lead to degradation of the celluloses' macromolecules exhibiting strongly modified material properties due to the reduction of the degree of polymerization [1]. The progress of the cellulose fibers oxidation was monitored by viscosimetric molecular weight determination.

## Materials

Natural cellulose fibers (cotton fibers Egypt Giza, type Pirate: fiber length 35 mm, micronaire value 4.1, regain 8.2 %) were investigated.

*a) Purifying treatments of cotton cellulose.* The following purifying processes for the cotton cellulose fibers were applied in order to obtain a well-defined reference substance:

*Boiling-alkaline cleaning* (NaOH). Removal of non-cellulose compounds (hemicellulose, waxes, pectin, proteins); 20 g/l NaOH, pH = 11.5, T = 95 °C, t = 90 min.

*Oxidative bleaching* (H<sub>2</sub>O<sub>2</sub>). Degradation of natural dyes and pigments; 9.5 g/l, 35 % H<sub>2</sub>O<sub>2</sub>, pH = 11.2, T = 95 °C, t = 30 min.

*Deminerlization* (HCl cleaning). Removal of all non-cellulose components (cations); 0.1 M HCl, T = 20 °C, t = 2 h.

After each treatment the fibers were washed with distilled water until a conductivity of less than

3mS/m was reached. The processed material was air-dried. Pre-treated cellulose fibers were chemically modified by oxidation.

#### b) Oxidation of cellulose fibers

*Selective oxidation.* Purified (according to the description under “a”) cellulose fibers were first oxidized with 0.01 M  $\text{KIO}_4$  at 20 °C for 6 h and 24 h to form aldehyde groups at  $\text{C}_2\text{-C}_3$  [1]. During the following process step, chlorite (III) selectively oxidizes the aldehyde groups to carboxyl groups [1]. The fibers were, therefore, treated with solutions of sodium chlorite (0.2 M) for 24 h at 20 °C under acid conditions at pH = 6 (100 ml of oxidation reagent per gram of fiber).

*Non-selective oxidation:* fibers were oxidized with 0.1 M  $\text{HClO}_4$  for 24 h and 48 h at 20 °C (100 ml of oxidation reagent per gram of fiber).

The oxidized fibers were washed with distilled water to constant conductivity and dried in air. The fiber bundles were taken apart to single fibers prior to the titration. Table 1 gives an overview about the applied chemical treatments of cotton cellulose fibers.

#### Analytical methods

*Titration method.* An air-dry sample equivalent to 0.5-1.0 g was weighted into a 200 ml glass-stopper flask. 100 ml of calcium acetate solution were added. The flasks were shaken overnight, and then the suspension of fibers was filtrated [1]. A suitable volume of filtrate was pipetted into a beaker and the color indicator murexide was added as a metalchromic indicator. The pH value of the filtrate was adjusted to 12 by the addition of 0.1 M sodium hydroxide solution. The decrease in concentration of calcium acetate solution after contact with the fibers was determined using an automated titrator Mettler Toledo DL 53. 0.1 M EDTA solution was used as a titrant (standardization against zinc sulfate). The equivalence point was indicated photometrically using a Mettler Toledo DP 660 phototrode, which measured the absorbance of the solution after each addition of titrant volume (V) and, therefore, color changes at the equivalence point were perceived automatically as well as visually. The process was observed using a potentiometric unit. The equivalence point was determined from the classical titration curve  $E = f(V)$  by non-linear regression analysis [7]. The carboxyl group content of the cellulose sample is obtained according to:

Sample	Treatment of cotton cellulose fibers (Egypt Giza 86, type Pirate)	Type of treatment
A	Pre-treated (alkaline boiling and oxidative bleaching) and demineralized fibers	Purification
B	Sample A was oxidized by 0.01 M $\text{KIO}_4$ , T = 20°C, t = 6 h and then treated with: 0.2 M $\text{NaClO}_2$ , T = 20°C, t = 24 h, pH = 6	Selective oxidation
C	Sample A was oxidized by 0.01 M $\text{KIO}_4$ , T = 20°C, t = 24 h and then treated with: 0.2 M $\text{NaClO}_2$ , T = 20°C, t = 24 h, pH = 6	Selective oxidation
D	Sample A was oxidized using: 0.1 M $\text{HClO}_4$ , T = 20°C, t = 24 h	Non - selective oxidation
E	Sample A was oxidized using: 0.1 M $\text{HClO}_4$ , T = 20°C, t = 48 h	Non - selective oxidation

T = temperature of treatment [°C], t = time of treatment [hours]

**Table 1.** Chemical modification of cellulose fibers

$$COOH = \frac{(V_{eqb} - V_{eqa}) \cdot C \cdot f \cdot 1000}{m} \quad (1)$$

[mmol/kg]

where  $V_{eqa}$  is the consumption of titrating reagent (EDTA) for the sample [ml],  $V_{eqb}$  is the consumption of titrating reagent (EDTA) for the blank value [ml],  $C$  is the concentration of the titrating reagent [mol/l],  $f$  is the factor of the titrating reagent, and  $m$  represent the weight of sample [g]. All presented values are the mean value of 5 parallel measurements.

**Methylene blue adsorption.** A weighted cellulose sample (approx. 0.5 g) of known water content was suspended in 25 ml of aqueous methylene blue chloride solution (300 mg/l) and 25 ml of borate buffer of pH = 8.5 for 1 h at 20 °C in an 100 ml Erlenmeyer flask and then filtered through a sintered-glass disk. 5 or 10 ml of the filtrate were transferred to a 100 ml calibrated flask. Then 10 ml of 0.1 N HCl and subsequently water, up to 100 ml, were added and the methylene blue content of the liquid was determined photometrically, employing a calibration plot. The total amount of free, i.e. non-adsorbed, methylene blue was calculated from experimental results (A) [8]. Applied analytical equipment: Perkin spectrophotometer, Elmer Lambda 2 UV/VIS. The carboxyl group content of the sample is obtained according to [8]:

$$COOH = \frac{(7.5 - A) \cdot 0.00313}{E} \quad (2)$$

[mmol/g]

where  $A$  is the total amount of free methylene blue [mg] and  $E$  is the weight of oven-dry sample [g]. All presented values are the mean value of 5 parallel measurements.

**Viscosimetric determination of the degree of polymerization.** The degree of polymerization was determined viscosimetrically after dissolving the cellulose samples in EWNN

(sodium salt of ferric tartaric acid) according to standard DIN 54 270 [9-11]. The viscosity measurements were performed in a modified Ubbelohde viscometer (capillary length 78 mm, capillary diameter 0.75 mm, 0.7 cm<sup>3</sup>). The intrinsic viscosity  $[\eta]$  was calculated from the efflux time of the cellulose solution ( $t$ ), the blank EWNN solution ( $t_0$ ), and from the concentration of cellulose in solution ( $c$ ) according to the Schulz-Blaschke equation [12]:

$$[\eta] = \frac{(\eta_{rel} - 1)/c}{1 + k_{\eta} \cdot (\eta_{rel} - 1)} \quad (3)$$

where  $\eta_{rel}$  is the relative viscosity and  $k_{\eta}$  is the coefficient for a given polymer solvent system ( $0.3 < k_{\eta} < 0.4$ ). The degree of polymerization (DP) was calculated according to Kuhn, Mark, Houwink [13]:

$$\overline{DP}_{\eta}^{\alpha} = \frac{1}{K_p} \cdot [\eta] \quad (4)$$

where  $K_p = 33 \cdot 10^{-3}$  [dl/g] and  $\alpha = 0.74$ .

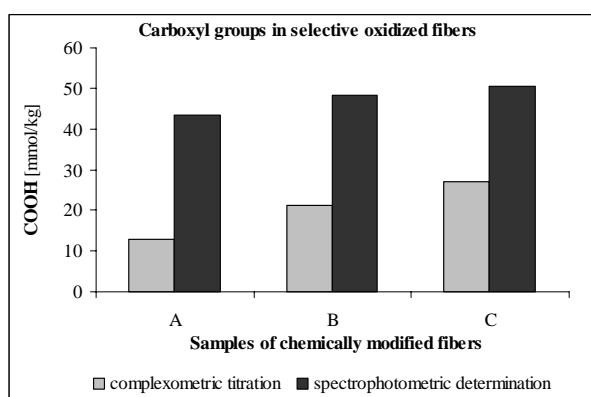
## Results and discussion

The values of the carboxyl group content obtained by the titration technique for different chemically modified samples are presented in Table 2 and compared with the values obtained using the methylene blue method.

Sam ple	Titration method [mmol/kg]	CV [%]	Methylene blue method [mmol/kg]	CV [%]
A	12.81	2.28	43.26	0.27
B	21.36	2.50	48.25	0.31
C	26.91	4.75	50.44	0.50
D	32.10	4.20	54.0	1.10
E	39.64	6.92	57.50	0.2

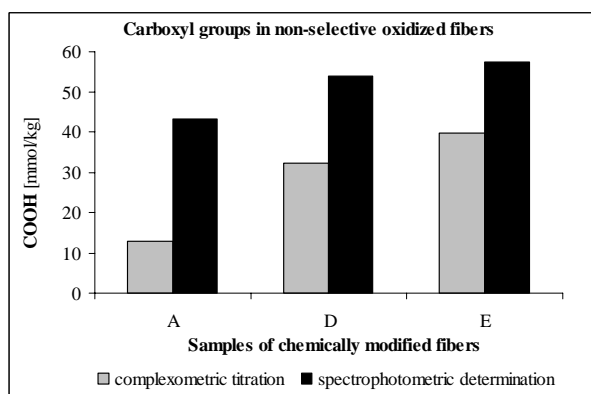
**Table 2.** Carboxyl content of chemically modified cotton fibers measured using titration method and methylene blue method; CV is coefficient of variation

The reference material A (purified) has a carboxyl group content of 12.8 mmol / kg obtained by complexometric titration and 43.26 mmol / kg  $-COOH$  groups obtained by the methylene blue method. The differences in the absolute values obtained using complexometric titration and spectrophotometric determination will be discussed in detail later. The ion exchange capacity of the fiber increased after the oxidation processes due to increased quantity of carboxyl groups. An evaluation has been made about the effect of oxidation time and reagent concentration on the oxidation process.



**Figure 1.** Carboxyl group content in selectively oxidized fibers (B, C).

Figure 1 and Figure 2 show comparisons of the carboxyl group content for selectively and non-selectively oxidized fibers, which were determined using complexometric titration and methylene blue methods.



**Figure 2.** Carboxyl group content in non-selectively oxidized fibers (D, E).

### *Selective Oxidation (Figure 1)*

As discussed before, aldehyde groups are formed during the first step of selective oxidation at the  $C_2$ - $C_3$  positions, and in a second reaction step these aldehyde groups are oxidized to carboxyl groups. An increase in the  $-COOH$  group content determined using complexometric titration was observed in samples B and C, which were selectively oxidized to the aldehyde groups in 0.01 M  $KIO_4$  medium for different periods of time (sample C was oxidized 18 hours longer than sample B). Further oxidation to carboxyl groups was carried out during the same time (24 h) at a concentration of 0.2 M  $NaClO_2$ . The carboxyl group content of sample B (mmol / kg) has almost doubled compared to the reference sample A. The carboxyl group content of sample C is 26 % higher than that of sample B, which is a consequence of the higher amount of aldehyde groups gained in the first process step (increased treatment time: 24 h instead of 6 h). It is also difficult to determine whether all reducing groups in the cellulose have been oxidized to carboxyl groups.

### *Non-selective oxidation (Figure 2)*

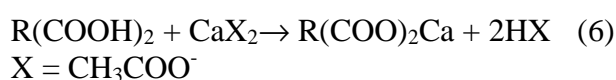
Under conditions of non-selective oxidation (treatment with 0.1 M  $HClO_4$ ) the carboxyl group content of fibers increased from 12.81 to 32.10 mmol / kg (D) in 24 hours, and to 39.64 mmol / kg (E) after 48 hours. The content of carboxyl groups in sample E (which was oxidized for 48 hours) is about 23 % higher in comparison with fibers oxidized for 24 hours (sample D). The increase of the carboxyl group content is more pronounced by non-selective oxidation in comparison with selective oxidation. On average a 50 % higher number of  $-COOH$  groups is observed compared to the values obtained by selective oxidation, where the oxidation mechanism is known. Using non-selective oxidation, any possible oxidation product may occur because the course of the oxidation process is unpredictable. A mixture of

products is present, oxidized to different degrees and according to different mechanisms. The degree of chemical modification of cellulose polymers depends on the reagent concentration and treatment time, which is also confirmed by literature data [1]. The spectrophotometric methylene blue method shows the same absolute tendency of those results at higher values (Table 2).

### Comparison of both methods

The results of  $-\text{COOH}$  groups content obtained by both methods (complexometric titration and spectrophotometric determination) indicate a severe discrepancy. The carboxyl group content determined by the methylene blue method is almost twice as high as that determined by the titration method. When seeking an explanation for these differences several assumptions are possible:

a) The interpretation of carboxyl content determination in cellulose by the  $\text{Ca}^{2+}$  exchange method is difficult due to the fact that stoichiometry is unknown. Two reactions of the divalent ions with carboxyl groups are possible [14-15]:



In reaction (5), one calcium ion is bound per carboxyl group. In reaction (6), one-half calcium ion is bound per carboxyl group and, therefore, a lower content of carboxyl groups is perceived in comparison with one-valence binding of dye (methylene blue) cations to carboxyl groups [1]. Mixed reaction types for the carboxyl groups content might also be possible, which is between both limit values. Regarding the literature [1], the results of methods based on monofunctional reaction mechanism may give the same values as methods based on bifunctional reaction mechanism. The affinity of  $\text{Ca}^{2+}$  ions toward

carboxyl groups is lower than the affinity of methylene blue dye cations [16].

b) Another explanation for the higher values of the methylene blue method is that fibers can react in two ways with the dye cations. Besides monofunctional reaction of methylene blue dye cations with carboxyl groups of cellulosic fibers, interactions with hydroxyl groups are also possible [1]. A study of the reaction mechanisms of dyes with cellulosic fibers indicated that the majority of interactions are hydrogen bonds, not ionic bonds [17].

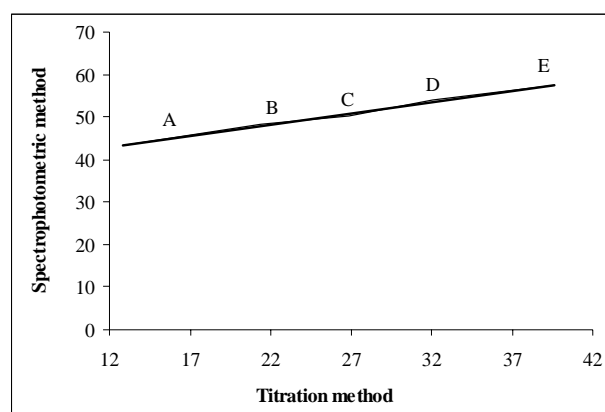


Figure 3. Correlation between methylene blue and titration methods.

The systematic error of the methylene blue method can be calculated by extrapolating the regression line in Figure 3, and amounts to 36 mmol / kg. It can be concluded that this amount of dye was non-specifically adsorbed (without interaction with carboxyl groups) at other accessible places in the non-crystalline region of the polymer. The smaller relative increase of  $-\text{COOH}$  content determined by the methylene blue method after oxidation processes is observed due to the larger systematic error. The methylene blue method is, therefore, less sensitive for monitoring changes of carboxyl groups after oxidation processes, which is confirmed by the slope of the correlation function ( $n = 0.5376 < 1$ ) between titration and spectrophotometric methods. It can be concluded that a bigger systematic error is obtained using the methylene blue method, but

a larger random error using the titration method. The less perfect repeatability of the titration method may be caused by the following facts:

- possible non-specific adsorption on the fiber surface,
- very low concentration of calcium acetate in the solution – large experimental error,
- quality of the water used during the processing operations (small amounts of different ions present in the distilled water causes lower ion-exchange values, because the fibers are incompletely turned into the protonated H-form using this water),
- atmospheric  $\text{CO}_2$  interferes with the determination (carbonate error).

Nevertheless, an excellent correlation between both methods is evident in spite of the different absolute results achieved (Figure 3). The correlation coefficient between both methods is approximately 1.

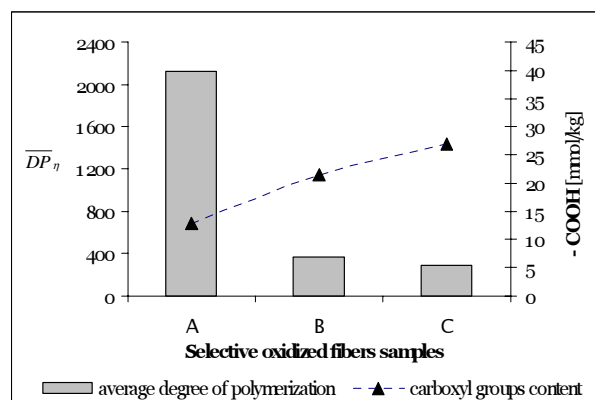
### Molecular structure changes

Chemical modifications of fibers also cause changes in carboxyl end groups and in the average degree of polymerization ( $\overline{\text{DP}}_\eta$ ). Precise information about products and reaction mechanisms among oxidation procedure can only be gained with a combination of both methods (complexometric titration for determination of  $-\text{COOH}$  groups and viscosimetric determination of  $\overline{\text{DP}}_\eta$ ). The results of determining the degree of polymerization using the viscosimetric method are given in Table 3.

Sample	$[\eta]$ [ml/g]	$\overline{\text{DP}}_\eta$	CV [%]
A	954,2	2117	4,82
B	259,6	365	1,60
C	219,2	290	2,31
D	990,8	2228	3,2
E	1014,7	2301	2,92

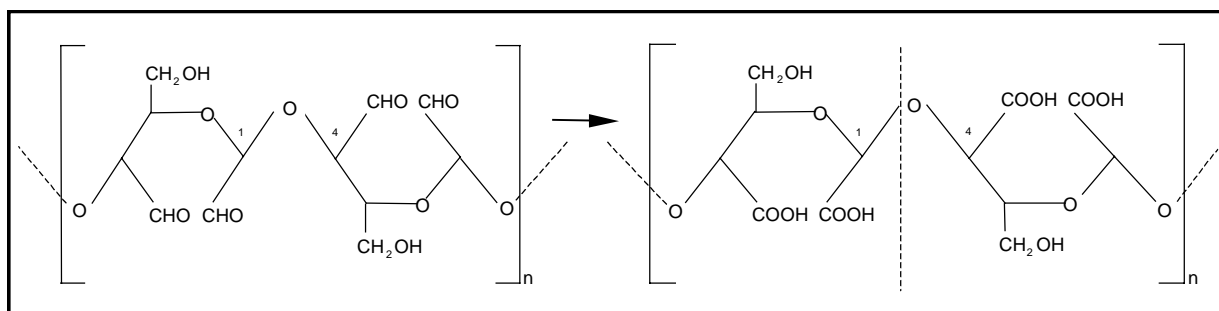
**Table 3.** The results of determining the intrinsic viscosity  $[\eta]$  and degree of polymerization  $\overline{\text{DP}}_\eta$  using the viscosimetric method, CV is coefficient of variation.

The oxidation processes lead to an increased content of carboxyl groups as well as to a cleavage of 1,4- $\beta$ -glycosidic bond giving shorter polymers chains. The literature states that oxidation with chlorites causes cleavage of polymer chains (Figure 4) giving new carboxyl end groups, which is confirmed by our results in the case of samples B, and C (Figure 5).

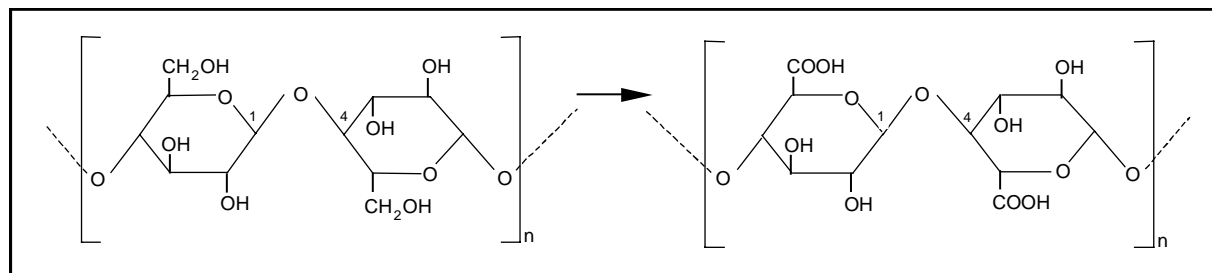


**Figure 5.** Degree of polymerization of selectively oxidized fibers (B, C).

Sample B gives a six times lower value of  $\overline{\text{DP}}_\eta$  (365) and sample C gives a seven times lower value of  $\overline{\text{DP}}_\eta$  (290) than the untreated sample A (2117), respectively. On average the  $\overline{\text{DP}}_\eta$  of the selectively oxidized fibers (samples B and C) decreased by about 90 % regarding the untreated sample A, and simultaneously the carboxyl group content increased by 88%, which indicates a direct relationship between the reduction of  $\overline{\text{DP}}_\eta$  and the increase of the carboxyl group content. The  $\overline{\text{DP}}_\eta$  of sample C decreased by a further 10% regarding sample B due to an 18 h longer oxidation time in the first phase of selective oxidation, which gave higher  $-\text{COOH}$  group content and more intensive cleavage of 1,4- $\beta$ -glycosidic bonds. Acid non-selective oxidation with 0.1 M  $\text{HClO}_4$  does not cause the cleavage of 1,4- $\beta$ -glycosidic bonds, and no reduction in chain length occurred. This indicates a mechanism of carboxyl end group formation with oxidation on  $\text{C}_6$  (Figure 6).

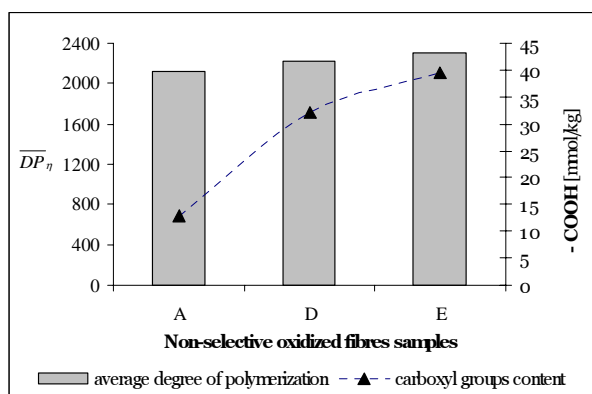


**Figure 4.** Schematic presentation of the mechanism of cellulose oxidation by chlorite (III)



**Figure 6.** Schematic presentation of the mechanism of carboxyl end group formation with oxidation at C<sub>6</sub>.

Therefore, the  $\overline{DP}_n$  values of non-selective oxidized fibers are only slightly higher (on average by about 7 %) than the  $\overline{DP}_n$  of the untreated sample (Figure 7). These minor differences can be due to random or systematic errors.



**Figure 7.** Degree of polymerization of non-selectively oxidized fibers (D, E)

## Conclusion

The influence of chemical modifications on the ion exchange properties was studied, which is linked with the number of carboxyl groups. Oxidation of cellulose fibers causes an increased amount of carboxyl groups. In

comparison with non-selectively oxidized fibers, selectively oxidized fibers show lower content in these groups (mechanism of oxidation). The methylene blue and the titration methods used for carboxyl group determination in oxidized fibers are in excellent correlation.

Complexometric titration is due to lower systematic error and higher sensitivity more appropriate for carboxyl group content determination than the spectrophotometric method, which is recommended as a comparable method to confirm any tendency of results obtained by complexometric titration. The results of this investigation demonstrate quite clearly that complexometric titration is an excellent tool for monitoring the influence of chemical modifications on the functional group content.

When the results of carboxyl group determination and the viscosimetric determination of  $\overline{DP}_n$  are compared, the following conclusions can be drawn: (a) the  $\overline{DP}_n$  of selectively oxidized cellulose fibers is decreasing equally with the increasing  $-COOH$  content, and (b) non-selective oxidation in an acid environment gives carboxyl groups at C<sub>6</sub> (from  $-CH_2OH$ ).

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## DETERMINATION OF CARBONYL FUNCTIONS IN CELLULOSIC SUBSTRATES

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The reliable and accurate determination of oxidized functionalities in cellulosic substrates still represents a largely unsolved problem in cellulose chemistry. Aldehyde and keto structures are “hot spots” along the cellulose chain, where further chain cleavage might occur. Carbonyls are also relevant for processes such as yellowing or aging. Conventional approaches (copper number, oxime or cyanohydrin method) provide sum parameters only and suffer from limited comparability. In our approach fluorescence labeling was chosen. Pulp samples are treated with a highly selective fluorescence label and are subsequently analyzed by size exclusion

chromatography. The method is applied as pre-column derivatization and allows the measurement of carbonyl profiles (plots DS vs. MW). Thus, the total carbonyl content and the differential mass distribution of pulps can be determined. Practical aspects of the newly developed method, a comparison of the approach to conventional methods, and different applications demonstrating the general scope of the method will be presented.

**Keywords:** cellulose, carbonyl group determination, carbonyl group profiles, fluorescence labeling, gel permeation chromatography (GPC), CCOA method

### Introduction

Cellulose is the most abundant polymer from renewable resources. While the chemical structure of the cellulose backbone does not seem to offer major challenges anymore, the supramolecular architecture of cellulose and its biosynthesis remain the prominent topics in today's cellulose research. However, cellulose is not only the “ideal” homopolymer, which is built up of anhydroglucose units linked by  $\beta$ -1,4-glycosidic bonds, it contains small amounts of various other, “irregular” structures, which are mainly oxidized groups. This applies especially to the material, which has undergone a number of process steps in the pulp and paper industries, and - albeit to a lesser extent - also to genuine, untreated cellulose. The reliable and accurate determination of those oxidized functionalities in cellulose represented a largely unsolved problem in cellulose chemistry.<sup>1</sup>

Oxidized groups in cellulose, such as keto and aldehyde groups,<sup>2</sup> are introduced by pulping and bleaching processes, according to the respective conditions chosen.<sup>3</sup> Especially bleaching – both chlorine-based and oxygen-based – is known to affect the integrity of the cellulose backbone by generation of oxidized positions and subsequent chain cleavage, which can be a result of both homolytic reactions, e.g. attack of oxygen or oxygen-derived radicals, and heterolytic processes, such as  $\beta$ -elimination. The creation of oxidized groups along the cellulose chain is thus a highly undesired process, as these positions constitute “hot spots” along the carbohydrate chain, where a pronounced chemical instability is introduced and where subsequent cleavage will primarily occur. Oxidized positions in cellulose are a main reason for strength loss and decreased performance parameters in textiles, paper and other cellulosic materials, they are chiefly

responsible for general aging processes of celluloses,<sup>4</sup> and are furthermore assumed to be the cause and promoter of thermal and light-induced yellowing processes.<sup>5</sup>

The determination of carbonyls in cellulose has to contend with several inherent difficulties. The extremely low average contents of carbonyls, which range in the order of  $\mu\text{mol} / \text{g}$ , require very sensitive means of detection since conventional, direct instrumental techniques, such as IR, Raman, UV, fluorescence or NMR spectroscopy, fail to report such minor amounts. Hence, a chemical method must be applied, in which the carbonyl structures are either "titrated" by a reagent, or converted in a suitable reaction into structures, which can then be monitored by traditional spectroscopic techniques.

Three conventional approaches to estimate the amount of cellulosic carbonyls are rather common: the copper number, applying copper (II) salts, which are reduced in turn and determined titrimetrically.<sup>6</sup> According to the oxime method<sup>7</sup> carbonyls react with hydroxylamine, and the carbonyl content is reflected for instance by the nitrogen content as determined by elemental analysis. The third approach aims at converting the carbonyls into cyanohydrins by reaction with cyanide.<sup>8</sup> All these approaches suffer from clear and distinct drawbacks, they are either based on conversions whose underlying mechanisms are far from being understood (copper number), they provide data which are only an indirect measure of carbonyls (copper number), or they suffer from strongly limited reproducibility (oxime and cyanohydrin method).

In our approach, we started from two prerequisites: first, fluorescence spectroscopy was to be used as the reporting technique, as it is as a highly sensitive technique, which allows the detection even of smallest amounts of oxidized structures. Second, the method to be developed should be implemented into GPC measurements of cellulose (with fluorescence detection), and thus not only provide the carbonyl content as a sum parameter, but a carbonyl group profile in relation to the molecular weight of the cellulosic material.

## Materials and methods

GPC measurements used the following components: online degasser Dionex DG-2410 and Gynkotek DG-1310, pumps: Kontron 420; puls damper, autosampler HP series 1100, column oven Gynkotek STH 585; fluorescence detector TSP FL2000; MALLS detector Wyatt Dawn DSP with argon ion laser ( $\lambda_0=488\text{nm}$ ), RI detector Shodex RI-71; Data evaluation was performed by the standard Chromeleon and Astra software. For GPC measurements, the system as described by Schelosky *et al.*<sup>9</sup> was modified, see Figure 1 for the experimental setup. DMAc / LiCl (0.9 %, m/V), filtered through 0.02  $\mu\text{m}$  filter, was used as the eluant. The sample was injected automatically, chromatographed on four serial GPC columns and monitored by fluorescence (exc. 290 nm, em. 340 nm), MALLS, and refractive index (RI) detection. Molecular weight distribution and related polymer-relevant parameters were calculated by software programs, based on a refractive index increment of 0.140 mL / g for cellulose in DMAc/LiCl (0.9 % m/V).

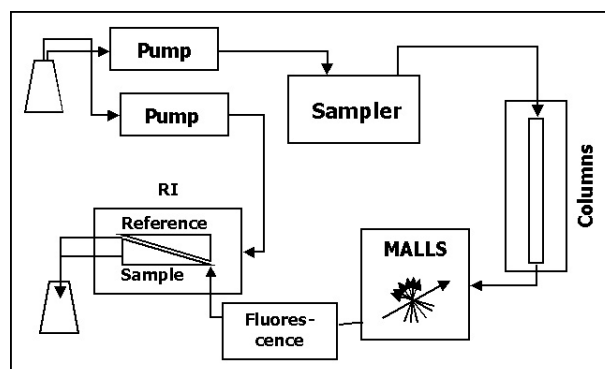


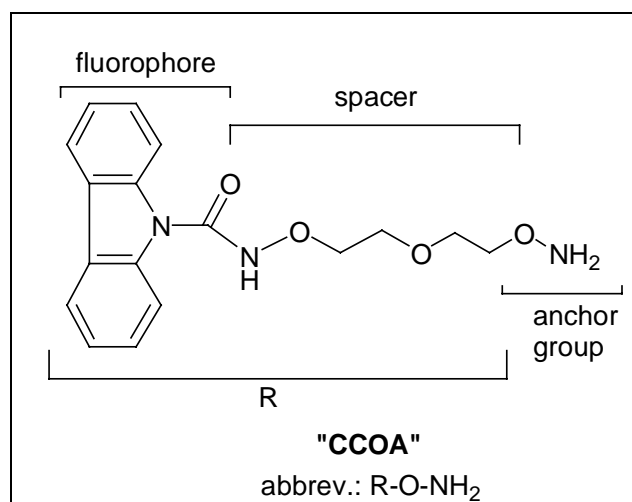
Figure 1. Setup of the GPC system used.

## Results And Discussion

*Method development.* The selection of the fluorophore in the fluorescence label depends strongly on the conditions of the GPC measurement. As MALLS (multi-angle laser light scattering) detection is indispensable, the fluorescent light must not interfere with this detection mode, which means that the difference between emission wavelength of the label and working wavelength of the laser used ( $\lambda_{\text{MALLS}} = 488 \text{ nm}$ ) should be as large as

possible. This is all but trivial, since most of the common, commercially available markers do not meet these requirements.

In recent literature, *O*-substituted hydroxylamines have been described as structures for carbonyl markers having increased reactivity as compared to hydrazines.<sup>10</sup> However, the fluorophores used, dansyl and rhodamine B derivatives, were inappropriate, due to their emission wavelengths interfering with MALLS detection. For that reason, a novel carbonyl-selective fluorescence label, which meets the requirements addressed above, was synthesized in an expeditious three-step approach as described previously.<sup>11</sup> The marker, termed "CCOA" according to its trivial name carbazole-9-carboxyloxyamine, is based on the fluorophore carbazole, with its fluorescence emission of 346 nm in DMAc / LiCl (0.9 % m/V) at an excitation of 290 nm being sufficiently remote from the working wavelength of the MALLS laser. As additional advantages, CCOA offers the reactive *O*-substituted hydroxylamine structure as the anchor group, which binds to carbonyls as an oxime, and carries an ethylene glycol spacer that ensures the fluorescence characteristic to be independent of type and environment of the group labeled.

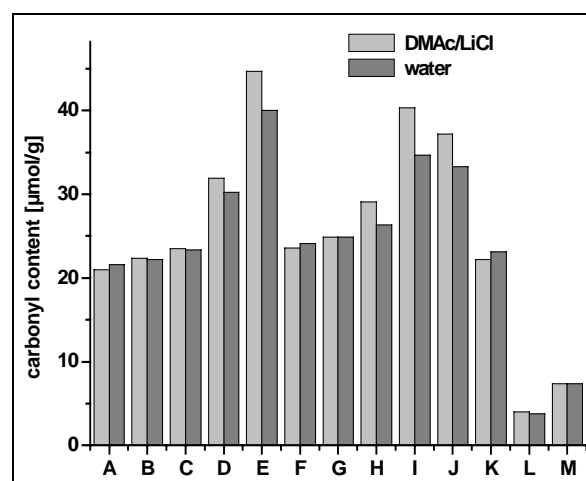


**Scheme 1.** Structure of the fluorescence label carbazole-9-carboxylic acid [2-(2-aminoxy-ethoxy)-ethoxy]-amide, "CCOA".

By means of model compounds, such as cyclohexanone as well as selectively oxidized carbohydrates as keto sugar models<sup>12</sup> and oligosaccharides with reducing end groups, it was demonstrated that CCOA reacts quantitatively with keto and with aldehyde groups.<sup>11</sup> All labeled model compounds exhibited identical

fluorescence emission maxima in this solvent. With the demonstration of the suitability of CCOA as a fluorescence label for keto and aldehyde groups in low-molecular, oxidized sugar units under the conditions needed for the chromatography of cellulose, the fundament was laid for the labeling of carbonyl structures also in macromolecular cellulosic materials.

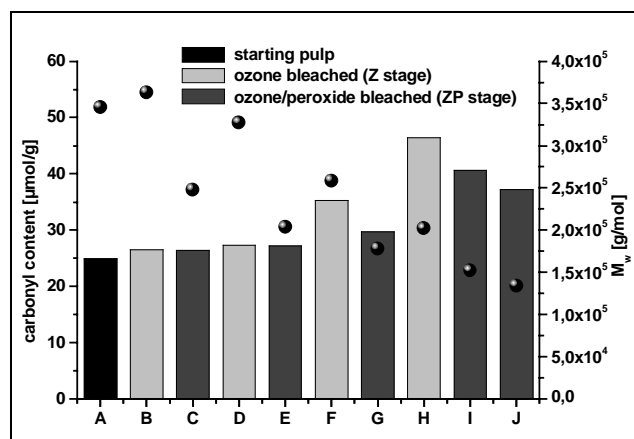
A complete derivatization is a prerequisite for the quantification of carbonyl groups in pulp. The derivatization procedure was optimized for a homogeneous solution in DMAc / LiCl (2.5 %, m/V) and an aqueous suspension of the pulps.<sup>13</sup> In the homogeneous working procedure the activated pulp was dissolved in DMAc / LiCl (9 %, m/V), diluted to a LiCl content of 2.5 % (m/V), and finally subjected to labeling with CCOA. The pulp was precipitated with water, thoroughly washed to remove excess label, activated, and re-dissolved for GPC analysis.



**Figure 2.** Comparison of the homogeneous and the heterogeneous labeling procedure: overall carbonyl contents determined. A: BS EO; B: BS Z1; C: BS Z2; D: BS Z3; E: BS Z4; F: BS Z1P1; G: BS Z2P2; H: BS Z3P3; I: BS Z4P4; J: BS Z4P5; K: BS; L: cotton linters; M: eucalyptus PHK. Abbreviations: BS = beech sulfite, E = E stage (extraction), O = oxygen stage, Z = ozone stage, P = peroxide stage, PHK = prehydrolysis Kraft; numbers reflect the intensity of the respective treatment.

As an alternative to the labeling in homogeneous phase, also the applicability of heterogeneous labeling in aqueous media was tested. Heterogeneous derivatization would circumvent the time-consuming and laborious removal of excess marker by precipitation and re-dissolution of the labeled pulp, and thus allow much shorter times for analysis.

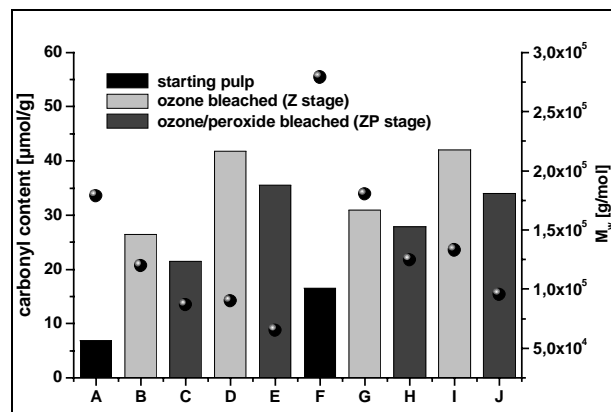
The optimized homogeneous and heterogeneous derivatization reactions were comprehensively compared by evaluating  $M_W$  and  $M_N$ , the peak form of the fluorescence signal and the overall carbonyl content. Both the heterogeneous and the homogeneous approach nearly produced the same values. This was demonstrated for a variety of different pulps, some examples are shown in figure 2. In some rare cases, the carbonyl content determined in water ranged up to 10 % below the values determined by homogeneous labeling, which can be attributed to restricted accessibility or inaccuracy problems in the respective sample. By comparing the  $M_W$  and  $M_N$  values of the non-derivatized and derivatized pulps, it was shown, that no chain degradation occurred during the derivatization procedure.



**Figure 3.** Overall carbonyl content (bars) and  $M_w$  (bullets) of a beech sulfite (BS) pulp, measured along a bleaching sequence with ozone and ozone/peroxide, respectively. A: BS EO; B: BS Z1; C: BS Z1P1; D: BS Z2; E: BS Z2P2; F: BS Z3; G: BS Z3P3; H: BS Z4; I: BS Z4P4; J: BS Z4P5. Abbreviations: Z = ozone stage; P = peroxide stage; increasing numbers reflect increasing intensity of the respective treatment.

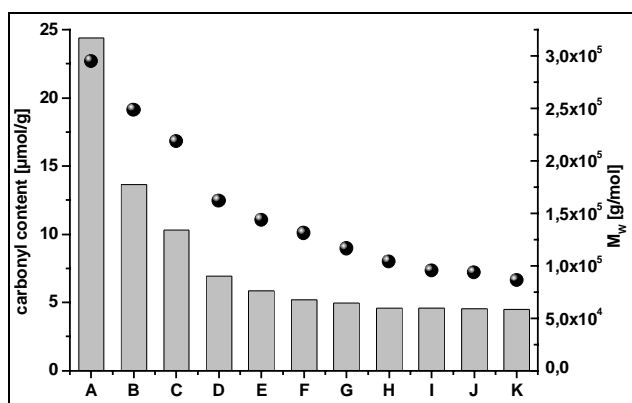
The heterogeneous labeling is advantageous over the homogeneous method for several reasons: it is completed at much shorter derivatization times, recording kinetics is unnecessary, the precipitation – re-dissolution procedure becomes obsolete, and the results are as consistent as those obtained according to the homogeneous working procedure. The heterogeneous method (and only this one) thus clearly has the potential to become a routine method in pulp and cellulose chemistry. The heterogeneous method was validated and applied in all following examples.<sup>14</sup>

*Analysis of the overall carbonyl content.* The ability of the CCOA method to determine the overall carbonyl content was used to monitor oxidative treatments of pulps. In the following some examples covering ozone/peroxide bleaching and alkalization are given.



**Figure 4.** Overall carbonyl content (bars) and  $M_w$  (bullets) of a spruce sulfite (SS) pulp and a eucalyptus prehydrolysis Kraft (PHK) pulp, measured along a bleaching sequence with ozone and ozone/peroxide, respectively. A: PHK; B: PHK Z1; C: PHK Z1P1; D: PHK Z2; E: PHK Z2P2; F: SS; G: SS Z1; H: SS Z1P1; I: SS Z2; J: SS Z2P2. Abbreviations: Z = ozone stage; P = peroxide stage; increasing numbers reflect increasing intensity of the respective treatment.

It was experimentally shown, that oxidative treatment of the pulps causes an increase in the carbonyl content, as expected. In ozone bleaching (“Z stage”), this increase was clearly dependent on the ozone charge. A subsequent peroxide treatment (“P stage”), comprising peroxide treatment and alkaline extraction, decreases the carbonyl content in turn. This is due to oxidative transformations of carbonyl groups and extraction of carbonyl-containing lower-molecular weight material, as is well known from bleaching chemistry. Figure 3 presents the data of bleached beech sulfite pulps, which had undergone different treatments with either ozone (Z) or ozone/peroxide (ZP). Likewise, figure 4 describes the bleaching of a spruce sulfite and a eucalyptus prehydrolysis Kraft pulp. Both figures clearly demonstrate that cellulose degradation, *i.e.* a DP loss, increases with increasing bleaching intensity, with ozone/peroxide combinations being especially critical.

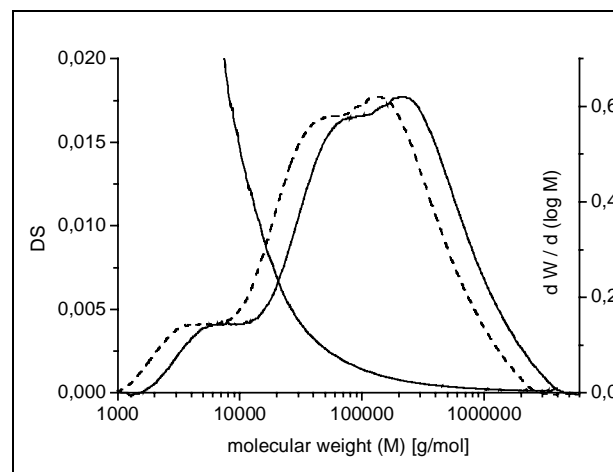


**Figure 5.** Overall carbonyl content (bars) and  $M_w$  (bullets) of a beech sulfite pulp, measured along alkalinization (18% NaOH, 42°C) along time. A: beech sulfite (starting material), B: after steeping; C: 1 h; D: 2 h, E: 3 h, F: 4 h, G: 5 h, H: 6 h, I: 7 h, J: 8 h, K: 9 h.

Steeping and aging of cellulose are important process steps in viscose fiber production. Steeping is mainly aimed towards the removal of residual hemicelluloses, whereas aging leads to appropriate pulp viscosities for further processing to viscose. Besides considerable changes in the molecular weight distribution during aging of alkali cellulose, also conversion of functional groups takes place. For the investigation of the effect of alkali treatment towards the carbonyl content, a beech sulfite pulp was treated with 18% NaOH. After pressing, the press cake was immediately shredded to provide an adequate surface area for a uniform reaction. Depolymerization kinetics at 42 °C was investigated. Samples were taken periodically and analyzed (figure 5). The carbonyl content decreased during the alkali treatment (steeping) by 50%. The carbonyl degradation slowed down with increasing reaction time and leveled off at 4 μmol/g. The main reason for the loss in CO groups is progressing oxidation to carboxyl functions.<sup>15</sup>

*Carbonyl group profiles.* If only the overall carbonyl content of a cellulose sample is considered – as important as this value might be – information is lost, since only a sum parameter is provided and possible differences between fractions of different molecular weight are leveled. Only carbonyl group profiles would convey the full amount of information. With the CCOA labeling having been elaborated into a general method, it became possible for the first time to determine the result of chemical

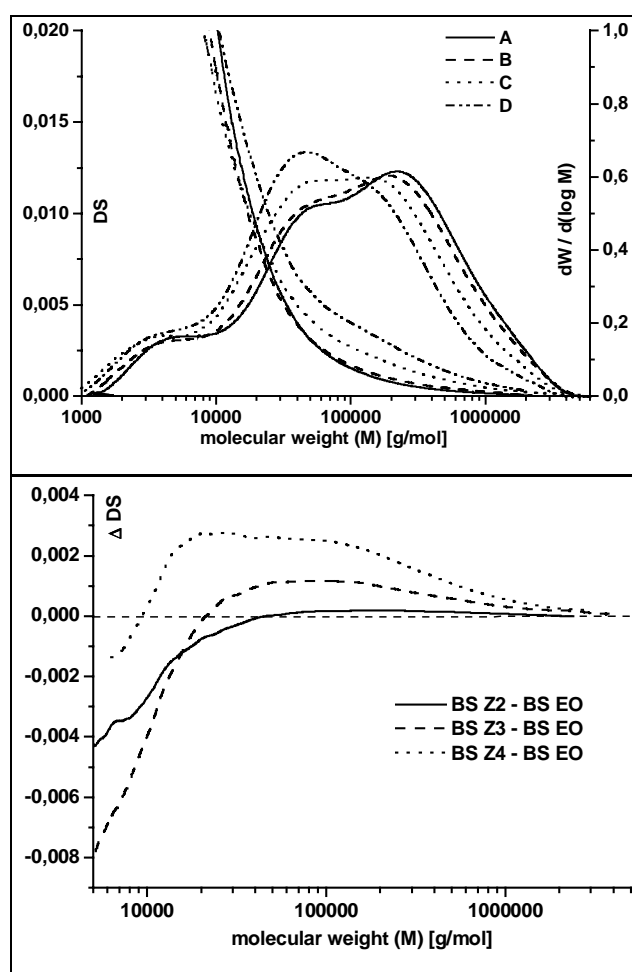
treatments of celluloses not only in terms of the overall carbonyl content, but also with regard to the carbonyl content relative to the molecular weight distribution. As the CCOA labeling is actually a pre-column derivatization procedure, the subsequent GPC analysis yields the carbonyl profiles for the respective samples, and reports possible changes in these profiles caused by chemical treatments.<sup>16</sup>



**Figure 6.** Carbonyl DS and differential MWD of a beech sulfite (BS), solid: unmodified, dashed: calculated MWD for a mild degradation without changes in the shape of the MWD.

In cellulose chemistry, the average degree of substitution (DS) denotes the number of substituted OH groups per anhydroglucose unit; it is most frequently used for cellulose esters or ethers. The DS thus reflects the completeness of a chemical modification at the hydroxyl groups of the polysaccharide. In the following, the term “carbonyl DS” shall be used to describe the average content of CO groups per anhydroglucose unit.<sup>17</sup> The typical decaying curve form (figure 6) of the DS graphs results from the higher number of reducing end carbonyl groups per anhydroglucose units in shorter chains. Especially ΔDS plots, which give simply the difference between two DS curves, facilitate the comparison of two samples with regard to their carbonyl contents relative to the molecular weight. They allow, for instance, to analyze in a very straightforward fashion, how a chemical treatment increases or decreases the carbonyl content in certain molecular weight ranges.

DS or  $\Delta$ DS plots on their own do not report changes in the overall carbonyl content. For that purpose, the MWD must be considered. Already from the natural content of reducing end groups, a DS can be expected for celluloses, which is decreasing with increasing MW. A shift of the MWD towards lower molecular weight at constant DS curve shape yields a higher overall carbonyl content (figure 6). This is caused by the changed ratios of low-molecular to high-molecular material, which are not considered for DS or  $\Delta$ DS curves. With MW degradation and a simultaneous decrease in DS, the effects on the overall carbonyl content are oppositely directed. An MW decrease causes an increase in overall carbonyl content, a shift of the DS curve leads to a decrease in the overall carbonyl content. Thus, regarding only the overall carbonyl contents means a loss of information.

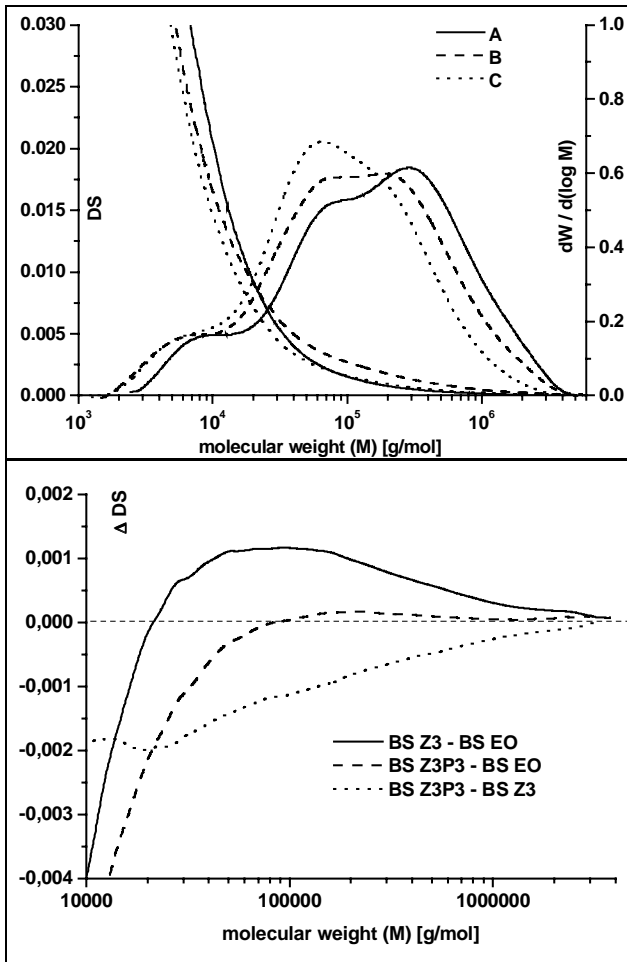


**Figure 7.** Carbonyl DS and differential MWD of a beech sulfite (BS) pulp after ozone-bleaching stages (Z). Increasing numbers reflect increasing intensity of the ozone treatment. A: starting pulp (BS EO); B: BS Z2; C: BS Z3; D: BS Z4.

A first example of the value of DS profiles is displayed in figure 7, which delineates the curves for ozone-bleached beech sulfite pulps. With increasing bleaching intensity, the carbonyl DS was increased for medium and high molecular weight regions, but dropped below the value of the starting material for low molecular weights. The boundary between DS increase and DS decrease ranged around an  $M_w$  of 10000 – 20000 g / mol. Thus, the ozone treatment is an interplay between carbonyl-generating and carbonyl-consuming processes. Such detailed descriptions of the carbonyl profiles would be impossible to make simply by the data for the overall carbonyl content.

Reducing end groups represent the major part of the total amount of carbonyl groups in cellulose chains with a low DP. Upon ozone treatment, these reducing end groups might be oxidized lactones and carboxylic acids, so that an ozone bleaching stage lowered the carbonyl DS in the lower molecular weight regions. In cellulose chains with a high molecular weight, however, the contribution of reducing end groups to the total amount of carbonyls becomes much smaller, so that the oxidation of reducing end groups is overcompensated by the introduction of new carbonyl functions. The generation of carbonyls predominantly into higher-molecular weight material might explain the well-known observation that ozone-bleached pulps suffer a severe DP loss in a subsequent P stage: when the carbonyls introduced upon ozone treatment are reduced by  $\text{NaBH}_4$ , the pulp is rendered largely insensitive towards the subsequent peroxide treatment.<sup>18</sup>

With the pulp used, a very low ozone charge did not significantly increase the carbonyl content, since preferably the residual lignin present in the material is attacked by the oxidant.<sup>19</sup> The progressing degradation of the polysaccharide material upon further oxidation, as reflected by the decreasing  $M_w$ , is clearly visible in figure 7.



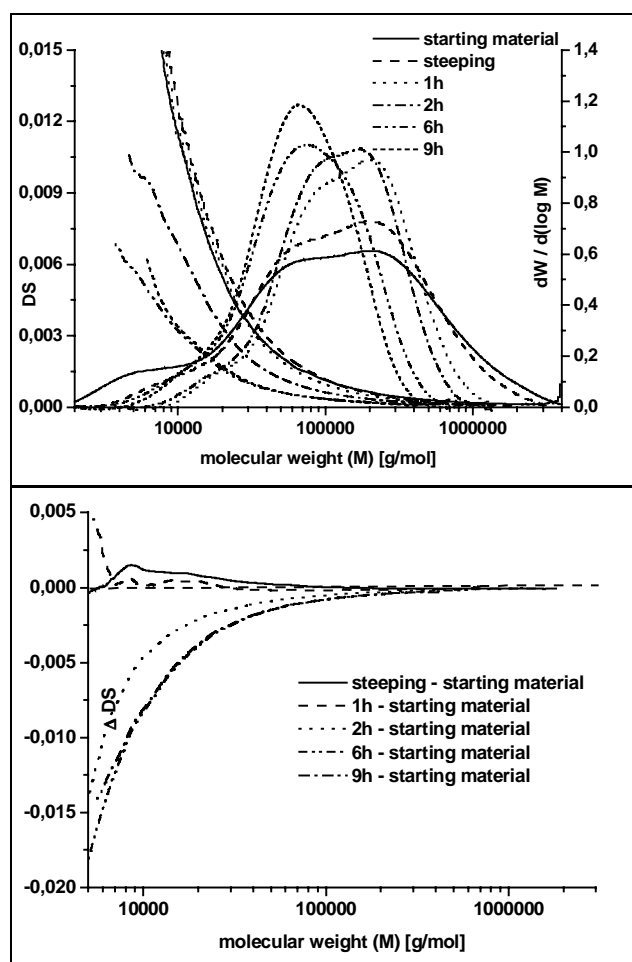
**Figure 8.** Carbonyl DS and differential MWD of a beech sulfite (BS) pulp after an ozone (Z) and a peroxide (P) treatment. A: starting pulp (BS EO); B: BS Z3; C: BS Z3P3.

The effect of a peroxide bleaching stage is demonstrated in the figure 8: a standard beech sulfite pulp was subjected to an ozone treatment followed by a peroxide bleaching stage. Again, it is obvious that the initial ozone treatment increased the carbonyl content at molecular weights above 20000 g / mol, and decreased it below this value. Also the DP loss is evident. The subsequent peroxide stage has a quite beneficial effect with regard to the CO content: in all molecular weight ranges the carbonyl content is decreased as compared to the ozone-bleached material. Moreover, the DS profile fell even below the level of the unbleached starting material at molecular weights below 70000 g / mol, and ranged only slightly above the curve for the initial pulp above 70000 g / mol. Nevertheless, the overall carbonyl content was slightly increased from 25 to 30  $\mu\text{mol} / \text{g}$  as a result of a shift of the MWD towards lower

molecular weights, which shows the limitations of this sum parameters with regard to a detailed interpretation of the results.

A comparison of the graphs for the starting pulp and the Z/P-treated pulp shows that this DP loss occurs predominantly in the higher-molecular weight region: the differential MWD curves below a MW of 10000 g / mol are nearly identical, whereas the curves above 10000 g / mol are shifted to lower values, *cf.* figure 8. Thus, the degradation produces mainly fragments of a molecular weight larger than  $10^4$ . This interpretation is justified since the yield loss upon bleaching is only 0.5% so that almost no material is lost. Thus, a chain cleavage occurs chiefly in the same molecular weight ranges, in which carbonyl groups are introduced during the ozone treatment. In the low MW range, which is only little effected by the Z stage, also the chain degradation is small.

Alkali treatment as performed in steeping and aging during the viscose production causes a decrease in the total carbonyl content. The most significant decrease (23.9  $\mu\text{mol} / \text{g}$  to 13.6  $\mu\text{mol} / \text{g}$ ) in carbonyl functions takes place during steeping. From the MW distribution and also from the carbonyl profile (figure 9) this can clearly be attributed to the dissolution of low MW parts of the pulp. No change in the DS profiles occurred during this stage. The same trend continues to up to 1 h aging time where still no changes in the DS profile in the cellulose polymer are observed. Between 1 and 2 h the carbonyls at higher MW parts are attacked as well, the drop between 10.3 to 6.9  $\mu\text{mol} / \text{g}$  can now be observed for the polymer backbone and not entirely be attributed to a dissolution process of low MW parts. Already at 6 h the decrease in carbonyl groups levels off, no significant changes are observed as compared to the final value.



**Figure 9.** Carbonyl DS and differential MWD of a beech sulfite (BS) pulp after alkali treatment (steeping and aging, 18% NaOH) with increasing reaction time. Treatment was performed at 42 °C.

## Conclusions

A novel analytical method for determination of carbonyl groups in cellulose by heterogeneous labeling with CCOA followed by GPC with fluorescence, RI and MALLS detection was developed. Already the overall carbonyl content is a valuable parameter to monitor the effect of oxidative chemical treatments. Furthermore, the method even provides carbonyl profiles relative to the molecular weight, which allow a much more precise evaluation of oxidative changes. Evaluation of carbonyl profiles can conveniently be done by means of “carbonyl DS” or “carbonyl  $\Delta$ DS” plots. Industrial relevant processes, such as bleaching and alkalization were investigated and the influence of these processes on the carbonyl content and on the carbonyl distribution of pulps was analyzed.

## Acknowledgment

The authors would like to thank Dr. Sonja Schiehser for technical assistance, and Dr. Susanne Jary and Dr. Andrea Borgards for preparing the samples of differently modified pulps. The financial support by the Austrian Christian-Doppler-Forschungsgesellschaft and Lenzing AG, Lenzing, Austria, is gratefully acknowledged.

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# THE BIOHOCH<sup>®</sup>-REACTOR: STATE OF THE ART IN BIOLOGICAL WASTEWATER TREATMENT IN THE VISCOSE FIBRE INDUSTRY

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A major development in our society has been taking place over the past years, and its pace is steadily accelerating: people have never been more aware of dangers for the environment - and hence for themselves. Governments are showing a great alertness for emissions of any kind, regulations imposed on the industry are constantly becoming stricter. Not only is environmental protection an increasingly growing cost factor, industry itself is agreeing on programs such as "Responsible Care" to fulfill its responsibilities as a key player in our natural and social environment.

To achieve a continuous and sustainable improvement in environmental protection, state-of-the-art technologies have been implemented. For the wastewater sector - especially in the viscose industry - the role of the leader in technology is filled by the BIOHOCH-reactor. Its low operational costs, high energy efficiency and high decomposition rates fulfill the expectations in every area and offer sound reserves in capacity and operational security. The following article should give you a deeper insight in its design and operation method.

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## Introduction

The discussion about the Best Available Technologies, now known under the term of BREF has been a permanent discussion since the 90s, when the industry made its commitment towards Responsible Care and also Sustainable Development. For example our chemical union defined a target to reduce on average the COD-load of 20 % within the next 10 years.

## Legal necessity

Within the European implementation of the IPPC regulations and the discussions about the BREFS some European members may see the necessity of acting.

The meaning of these abbreviations in exact wording is:

BREF = **B**est Available Technique **R**eference Documents. The BREF are discussed within the IPPC-regulations.

IPPC = **I**ntegrated **P**ollution **P**revention **C**ontrol.

This paper does not intend to give a report about the development of IPPC and the necessities resulting from the BREF, it presents an impression, how Best Available Technology could be defined on the wastewater sector. The BIOHOCH<sup>®</sup> reactor is surely not the only way to treat wastewater, but it is indeed a very good one.

## Historical development of wastewater treatment

Before going into the technical details a short overview about the history of wastewater treatment may be of interest. A proverb says, "Rome was not built in a single day"; its the same for the development of the BIOHOCH<sup>®</sup> reactor. Three development stages exist within the total process:

- 1963: Construction of a waste water pilot plant at the beginning of extensive trials for biological treatment of production wastewater
- 1967: Start-up of the unit I of the central biological waste water treatment
- 1977: Start-up of the unit II of the central biological waste water treatment
- 1981: Start-up of the unit III: BIOHOCH® reactor in Kelheim (the first in the world)
- 1991: the second BIOHOCH®-reactor went into operation.

We would like to highlight the year 1981: after 5 years of research time the first BIOHOCH® reactor in the world went into operation in Kelheim. 10 years of experience later, we built the second one in 1991 in a slightly different design.



**Figure 1.** Comparison between flat BOD-plant and the BIOHOCH® reactor.

## Waste water treatment – how does it work?

For better understanding the principles of wastewater treatment are explained and the details on the technologies involved are given.

As it is so often the case, nature itself played the role model for the sewage treatment system. In the narrow confines a full biological sewage treatment works, the same processes as in the natural water systems take place with high degree of efficiency. Everywhere there are harmless bacteria, which absorb the oxidizable organic substances dissolved in the water; the bacteria then transform the pollutants into harmless substances, such as carbon dioxide and water. The bacterial mass grows forming surplus sludge, which has to be removed for disposal.

## Principle of the BIOHOCH® reactor

To treat wastewater a few different technologies exist. To be able to understand the specifications of the BIOHOCH® reactor, Figure 1 shows you in an impressive way how different the two technologies are.

A BIOHOCH® reactor consists of a cylindrical tank, an activated sludge basin where the biological decomposition takes place, and a final sedimentation basin shaped like a inverted truncated cone surrounding the activated sludge basin (Figure 2).

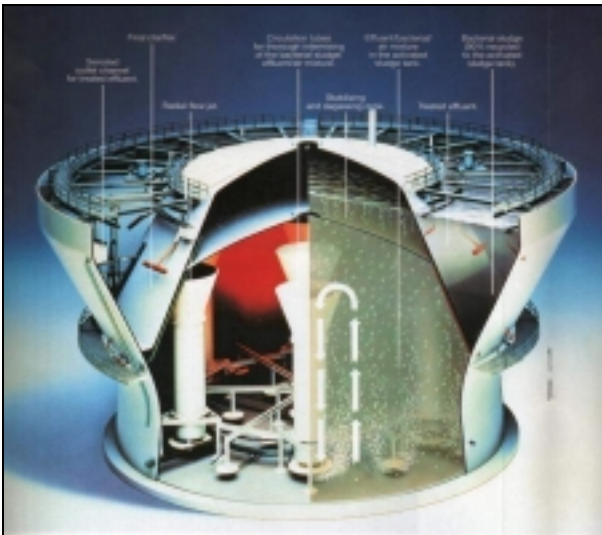
The oxygen required for the biological decomposition is taken from finely dispersed air. This is one of the great specialties of this BOD plant. The air is produced by screw compressors and injected through special nozzles at the bottom of the activated sludge basin.

In the final sedimentation basin the bacterial mass is separated from the cleaned wastewater by sedimentation. While the biggest part is returned to the activated sludge basin to re-continue its decomposition work, a small part is removed as surplus sludge. One of the advantages of this design is that it requires no sludge recycling pumps. A self-feeding current evolves due to the differences in density between the activated sludge basin (low density) and the final sedimentation basin (high density).

A further special feature of the BIOHOCH® reactor is that it has a simultaneous nitrification

and denitrification effect when the oxygen content of the activated sludge basin is set correctly. This is only of interest if you are dealing with mixed wastewater, such as that handled in Kelheim. Both viscose and acrylic wastewater are treated.

To get more security additional flotation units have been installed; each reactor is followed by these systems (Figure 3). Residual flakes are separated in four basins to produce a non-turbid outflow of purified water. This is achieved by injection of air. The air bubbles are adsorbing the sludge and transport it to the surface. A reamer system is removing the sludge from the surface.



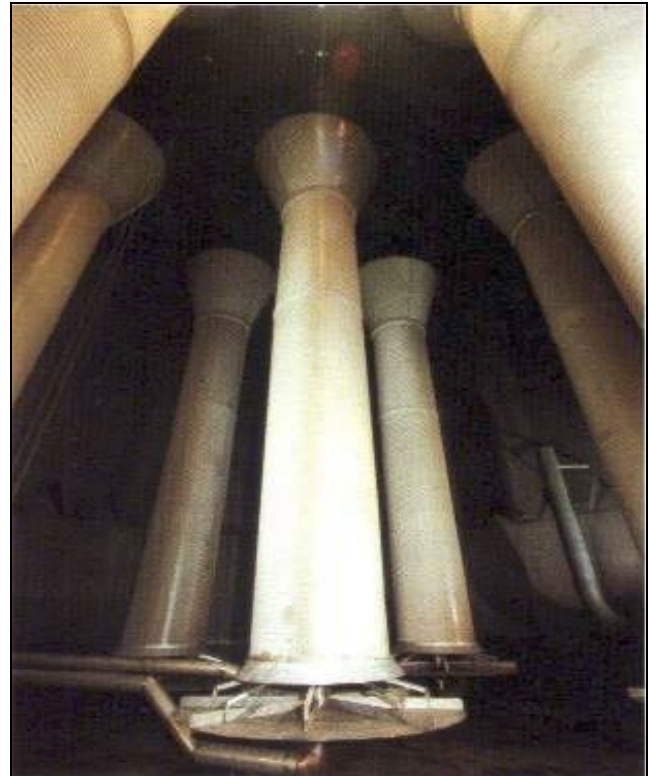
**Figure 2.** Structure of a BIOHOCH®-reactor.



**Figure 3.** Flotation system.

In the following, a short overview over the most important technical data is presented. Especially we want to point out the high COD-degradation and the low energy consumption.

By describing the BOD plant, the special air injection (Figures 4 and 5) was already mentioned. The central elements in any BIOHOCH reactor are radial-flow jets. These are two-component nozzles, in which the air is dispersed by a water jet, forming fine bubbles before being radially distributed by means of circulation tubes in the liquid to be aerated; this causes a uniform distribution over a large area.



**Figure 4.** Aeration system: jet circulation tubes.



**Figure 5.** Aeration system: radial flow.

Figure 6 shows the exact principle of this aeration system. Water is injected from the bottom, compressed air from the top. At the distribution plate we get fine dispersed bubbles. The higher the amount of injected air is, the finer become the bubbles. Fine dispersed bubbles have a large surface area and therefore guarantee extremely high oxygen utilization. In our first reactor (1981) we have also installed the so-called guiding-tubes. Our intention was

to achieve a better distribution of air by the optimized circulation. The 10 years of experience showed that this installation is not necessary. To describe the exact kinetic advantages would take too much space, but the principle behind them should be understood.

Figure 7 gives an impression what effect the BOD plant had on the effluent COD loads over the years. Smaller modifications in the process and at the BOD plant will be the key for a steady further improvement, as it is requested according to EMAS and Responsible Care.

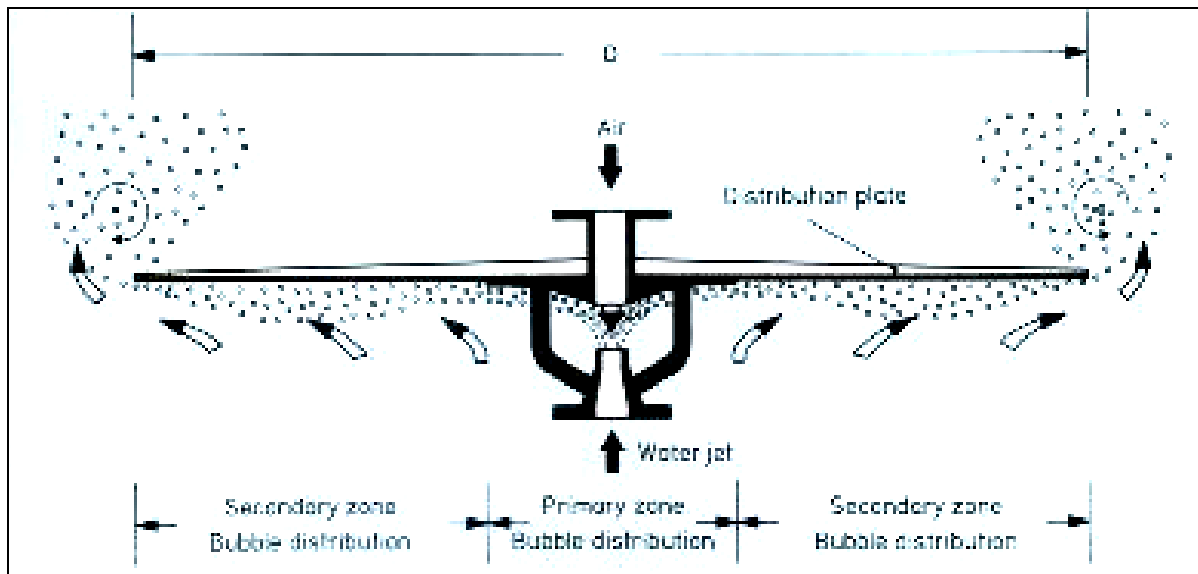


Figure 6. Principle of aeration system.

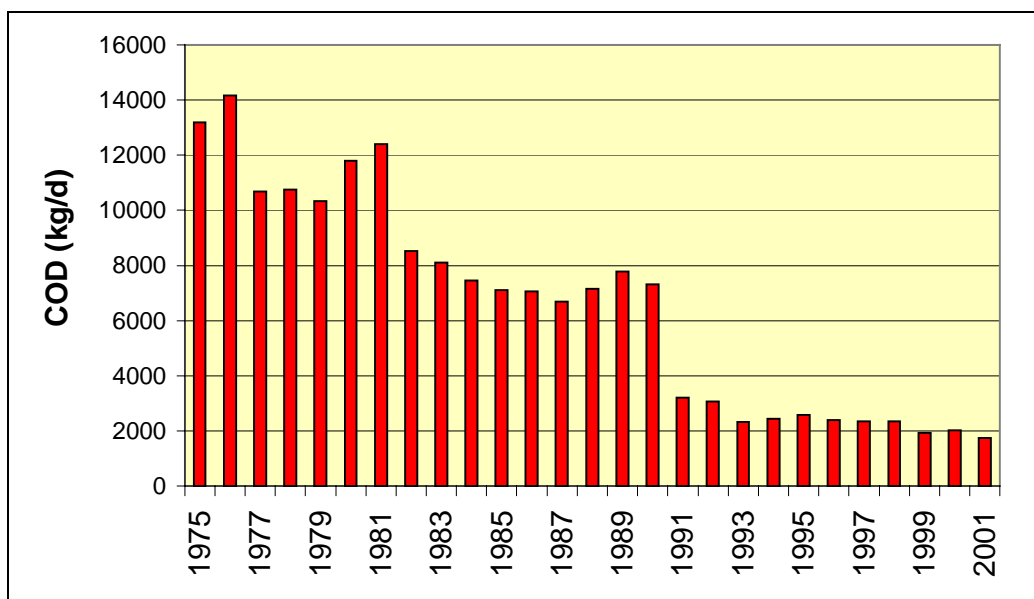


Figure 7. Development of the COD loads.

		<b>BHR 1</b>	<b>BHR 2</b>
<b>Height of liquid column</b>	[m]	15	15
<b>Capacity of activated sludge tank</b>	[m <sup>3</sup> ]	3.000	5.400
<b>Surface of final sedimentation basin</b>	[m <sup>2</sup> ]	250	550
<b>Capacity of final sedimentation basin</b>	[m <sup>3</sup> ]	1.450	3.810
<b>Max. sewage throughput</b>	[m <sup>3</sup> /h]	200	440
<b>Number of air injection nozzles</b>		7	21
<b>Max. total air input</b>	[m <sup>3</sup> /h]		10.000
<b>COD-load</b>	[kg/d]		15.000
<b>Oxygen utilization</b>	[%]		≈ 50
<b>Efficiency of decomposition COD</b>	[%]		≈ 95
<b>Efficiency of decomposition nitrogen</b>	[%]		≈ 80
<b>Energy consumption as a function of decomposed COD</b>	[kWh/kg]		≈ 0,8

**Table 1.** Technical data of the BIOHOCH reactor.

## Conclusion

The BIOHOCH<sup>®</sup>-reactor is a real alternative for all who aspire a satisfying and permanent solution on the wastewater sector. The final listing of advantages should emphasis this:

- High-rise design requires extreme little space,
- Short construction times mean economical installation,

- Optimum air injection based in radial flow nozzles,
- High degree of oxygen utilization saves costs,
- Minimum noise and odor nuisance,
- A freely accessible tank design that ensures optimum operational reliability.