

The origin and type of cellulose utilized in the manufacture of Nitrocellulose over the last thirty years

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Abstract

Purified cotton linters and softwood wood pulps are the main cellulose sources utilized in the manufacturing of nitrocellulose. At Rheinmetall Denel Munition cotton linters are solely used for the manufacture of military grades - and industrial grades nitrocellulose, where as softwood wood pulps are utilized for the manufacture of mining grades nitrocellulose. Cotton linters were purified in-house from 1971 until 2003. There after purified second cut cotton linters were imported from various suppliers. Softwood wood pulps from the South African paper industry were utilized for the manufacture of industrial and mining grade nitrocellulose.

During the in-house purification period mill run and second cut raw linters from the Southern African region, of which the exact growth area, cultivar of the cellulose as well as ginnery were known, had been utilized. The characterization and assigning of the linters to a specific type of nitrocellulose for utilization in solvent or solvent-less type of propellant manufacturing process was easier than in contrast to the current sourcing of purified linters from abroad.

In order to have fairly constant propellant manufacturing processes the quality of the incoming purified cotton linter from various suppliers needs to be controlled very accurately. When switching from one purifier/supplier to another the nitrocellulose manufacturing as well as the propellant manufacturing has to be re-qualified. Depending on the outcome of the results the further utilization of linters from a specific purifier/supplier has to be approved by the companies Material Revision Board. The characterization of the linters and the re-qualification methodology of all processes will be described.

For the manufacture of mining and industrial grade nitrocellulose softwood pulps were utilized as cellulose source. An overview of the characteristics of the wood pulp and the influence thereof on the nitration process and the quality of the nitrocellulose will also be given.

1. Introduction

Cotton linters have long been recognized as the main cellulose source for the production of military grades of nitrocellulose. Somchem Pty. Ltd. now part of Rheinmetall Denel Munition was founded on 1 November 1971. Since then nitrocellulose was manufactured in-house for use

in small, medium and large caliber gun propellants as well as double base rocket & missile propellant grains. This necessitated a cellulose source for nitration. The main cellulose source was mill run and second cut linters. The raw cotton linters were sourced from South African ginneries run by agricultural companies such as Clark Cotton and “Eastern Transvaal Cooperation”. When the annual supply of raw linters from South Africa was not sufficient additional raw linters were sourced from Zimbabwe or Zambia by Clark Cotton. At certain stages second cut raw linters were also imported from Turkey and Pakistan. The linters from Pakistan contained a lot of plastic fibers.

These mill run and second cut linters were purified in-house complying too DEF STAN and MIL-STD. The linter purification operations continued at the Rheinmetall Denel Munition’s Somerset West Site until 1985.

A new linter purification plant based on alternative manufacturing process technology was build and commissioned at the new Energetic Raw Material Manufacturing Site outside Wellington in 1984. The old plant was de-commissioned in 1985. Today the old plant has been demolished and the area rehabilitated.

With the new plant running smoothly a cellulose characterization project was started in 1987. The aim of this project was to determine the influence of the cultivar, production area and harvest year on the linter- and cellulose-homogeneity. This work continued up to 1991 and thereafter this information was utilized to channel certain raw cotton linters to a specific type of propellants. In 2003 the South African Ginning Industry decided to terminate all ginning of linters. A feasibility study concluded that it would be more economical to import already purified second cut linters.

After evaluation of linter samples from various overseas purifiers it was decided to utilize linters from Buckeye Germany (previously known as Temming linters). Unfortunately in 2005 Buckeye decided to close the German purification factory. At present we have three purifiers qualified where RDM can source purified linters from.

The situation of being totally in control of what was supplied to you as Nitrocellulose manufacturer (cultivar, cut length and precise growth area) changed to a situation where you can only test the incoming batches against the MIL STD and we all know that with these methods one does not really measure the variation in the linters due to nature.

Wood pulps were utilized for the manufacture of industrial and mining grade nitrocellulose. Later industrial nitrocellulose was also manufactured from second cut linters.

2. Discussions

2.1 Company History

Separate private companies where established long ago (1931, 1948 and 1971). Some off the business of these privately owned companies became part of ARMSCOR (Armaments

Corporation of South Africa) in 1971. In 1992 ARMSCOR split into Armscor – Procurement Agency for DoD and Denel Pty. Ltd. – Manufacturing Companies became Divisions of Denel. On 1 September 2008 Rheinmetall Denel Munition became effective.

2.2 Company Location and Production Facilities

Rheinmetall Denel Munition has five manufacturing sites two in the north of South Africa and three in the south. RDM's capabilities are from Raw Materials via Processed Products up to Integrated Systems.

The Wellington Site today manufactures energetic raw materials for the Propellant and Mining Explosives Industries. The linter purification plant as well as the Nitrocellulose manufacturing plant is situated at the Wellington Site.

2.3 History on the usage of different Cellulose sources

2.3.1 Wood pulp

Different types of cellulose sources are utilized for the manufacture of military nitrocellulose, industrial nitrocellulose for the paint and printing ink industry as well as for the mining industry. Traditionally only purified cotton linters as cellulose source are being used for military grade nitrocellulose. A lot of work on laboratory scale went into optimizing of South African wood pulps for the manufacture of industrial/lacquer grade nitrocellulose. Mining grade nitrocellulose (dynamite) was manufactured from slightly purified unbleached cotton linters. Industrial grade nitrocellulose (HX6/15) for the mining industry for the manufacture of Bound Nitrocotton was manufactured from South African softwood (Pine) wood pulp sheets (Kraft).

2.3.1.1 Optimization of South African wood pulps for use in lacquer grade Nitrocellulose

The general norm in the world in the 1980th and still today is to utilize Softwood wood pulps (Spruce wood) manufactured by the acid bisulphate process, (Calcium base) and bleached. Bleached pulp made by other means such as bisulphate process (sodium or magnesium base) or multistage sulphite process or perhaps sulphate process may be used. Some manufacturers nitrated the wood pulp in chip form and others in fluffed form. The difference in the nitration process of those two different physical forms lies in the mixed acid strength e.g. the nitric acid content of the mixed acids.

For fluffed wood pulp the mixed acids are very similar as for the military grade nitrocellulose. For chip form wood pulp the nitric acid content of the mixed lies above 50%. The physical characteristics of the wood pulp e.g. basis weight, thickness and apparent specific gravity are important criteria for certain stages in the nitration process. Chemical impurities such as iron, silica, lignin, pentosans and resin may affect the clarity and colour of the resulting cellulose nitrate solutions.

At that stage in South Africa the wood pulp manufacturing processes in combination with the type of wood (hardwood vs. softwood) differed from the typical situation in Europe.

Europe:	Softwood and sulphite process Hardwood and sulphate process
South Africa:	Softwood and sulphate process Hardwood and sulphite process

In 1984 there were two wood pulp manufacturers in South Africa

Sappi with the sulphate process utilizing softwood (Pine) for manufacturing of wood pulp sheets with a α -cellulose content of $\leq 88\%$, which is too low for the manufacture of good quality lacquer grade industrial nitrocellulose.

Saiccor with the sulphite process utilized a mixture of hardwood (90% eucalyptus and 10% wattle) to manufacture wood pulp sheets with a α -cellulose content of $\geq 92\%$. It was decided to utilize Saiccor wood pulp for laboratory scale experimental purposes.

At first experimentation was started with off the shelf Saiccor wood pulp sheets. These first experimental nitration runs indicated that the physical characteristics of the wood pulp sheets had to be changed and optimized. The thickness and density of the sheets were found to be important. These two parameters have an influence on the cutting characteristics and nitration ability, in other words the mixed acid composition, ratio of mixed acid to pulp, nitration time, yield, acid retention after nitration and finally the solution quality of the industrial nitrocellulose. These above mentioned parameters were used to optimize the physical characteristics of the wood pulp.

Together with South African wood pulp softwood pulp (Spruce) from Saugbrugs and Borregaard (Norway) was utilized for comparison purposes. These pulps were utilized by a European industrial nitrocellulose manufacturer.

Optimum physical parameters were found to be as follows:

Thickness of wood pulp sheets	:	0.77 ± 0.03 mm
Basis weight	:	600 ± 50 g/m ²
Packing density	:	0.78 ± 0.04 g/cm ³

The basis weight is determined by taking the mass at 65% humidity.

Saiccor pulp sheets with above mentioned characteristics nitrated for 2 to 2.5 hours with the following mixed acid composition e.g. HNO₃ 55%, H₂SO₄ 32.5% and H₂O 11.3% yielded industrial nitrocellulose with a nitrogen content of 12.02 %. The nitration temperature at the beginning of nitration cycle was 25°C and the temperature was increased to 45°C over the first hour of the nitration cycle, where after the nitration temperature was kept at 45°C for the rest of the nitration time.

A first order test to determine the solution quality was done by dissolving the industrial nitrocellulose in acetone. This gave a good indication of whether any under-nitrated fibers were present.

The imported Saugbrugs and Borregaard pulps gave similar results.

For the reason that no softwood pulp manufactured with the sulfite process was available in South Africa and importing European softwood pulp from Norway would be very costly, it was decided to utilize cotton linters in the industrialization of the manufacture of industrial nitrocellulose. Industrial nitrocellulose was manufactured at the Wellington Site nitration plant for \pm 5 years, utilizing cotton linters as the source of cellulose.

2.3.2 Cotton linters

Since inception of Armscor 1971 South African ginned cotton linters were purified in-house.

2.3.2.1 Linter purification at Somerset West Site

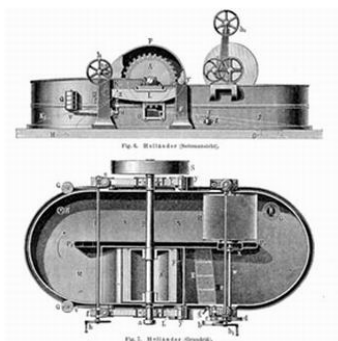
The old previous Somerset West Site linter purification process consisted of caustic extraction of all non-cellulosic material in a spherical rotating digester, washing the extracted linters in a type Hollander beater, bleaching and washing in a rotating bleaching drum, centrifuging, drying in an oven and bale pressing. The photos below illustrate the equipment that had been utilized 40 years ago by RDM. Some linter purification plants based on this older process technology are still up and running.



New spherical digester



Spherical digester in use



Linters washer/beater



Washing of extracted cotton linters



Bleaching and washing of cotton linters

Pictures from web www.ntyy.com

2.3.2.2 Cotton linter research project

In 1987 a linter characterization project was started. Raw cotton linter samples, identified by the cultivar, production area and harvest year' from each ginnery in South Africa were received. Qualitative and quantitative cellulose characteristics were selected to better describe the material. Characterization was done on raw and purified linter level.

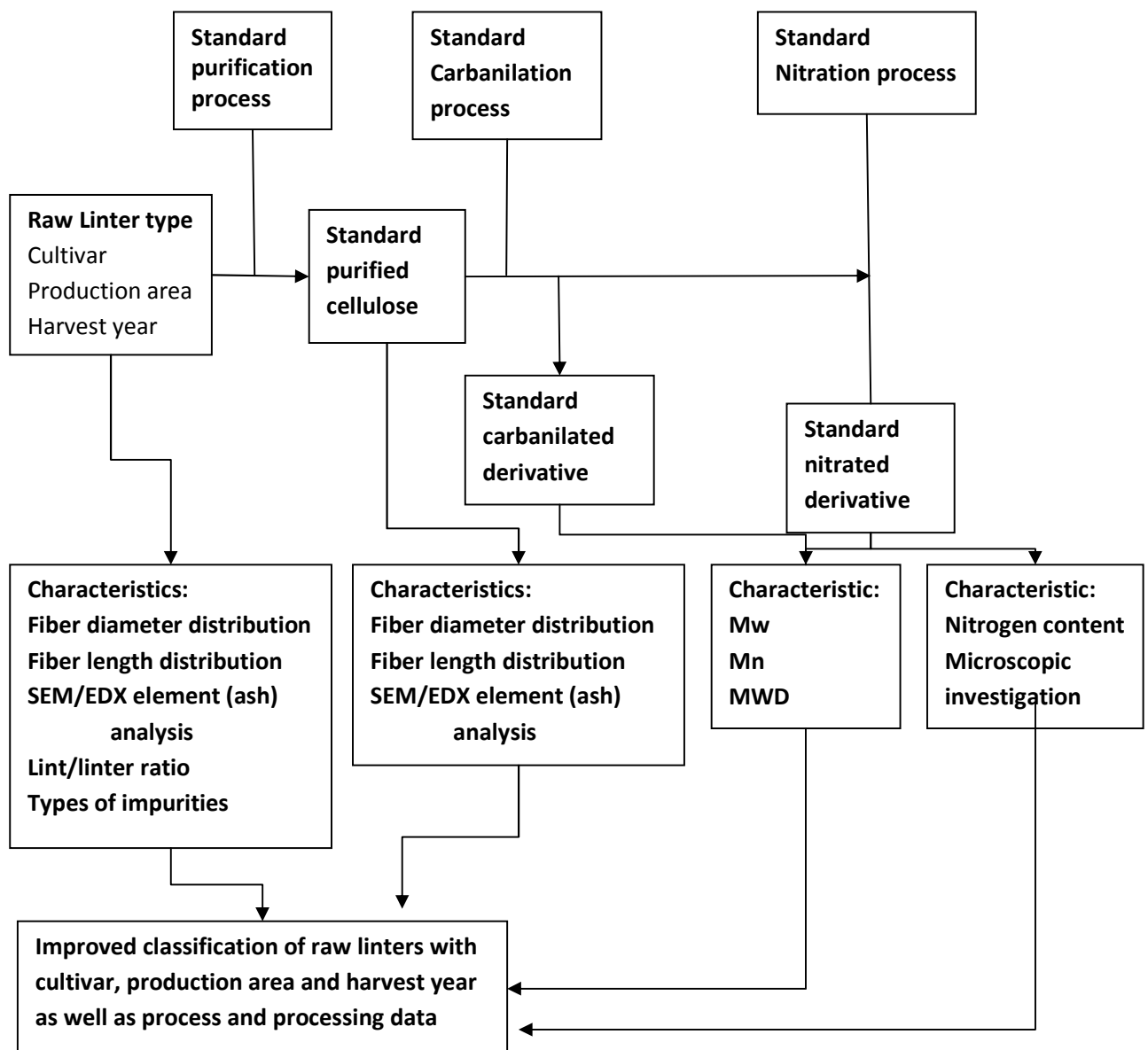
The raw linters were classified by fiber length distribution, impurities (leaf portions, seed-coat, husks, hulls and sand), ash content and fiber morphology (damaged fibers and fixing to seed-coat).

The raw linters from different production areas contain varying quantity impurities depending on whether the cotton was harvested by hand or machine. A Shirley trash Separator was utilized to

clean all linter samples in the same manner before chemical purification. The trash was characterized according to certain size fractions.

The mechanically purified linters were purified by the method of Dorée (The methods of cellulose chemistry, Charles Dorée, Chapman & Hall Ltd., 1933-Science). This method hardly degrades the cellulose and was used on all linter samples. Air dried linter samples were carbanilated on laboratory scale. The molecular weights and molecular weight distributions of the tricarbnilate were determined by gel permeation chromatography. The data was analyzed statistically.

The diagram below summarizes the whole characterization methodology.



The conclusion from the research work (1987 – 1991) is as follows:

Variation in the degree of polymerization, degree of substitution, fiber diameter, fiber length and elemental distributions of the South African produced cotton linters are of such magnitude that cotton linters of the various cultivar, production locality and production year combinations cannot be treated as a homogeneous source of cellulose.

The variation in the material and product characteristics can both be measured and their contributions to the total variation, determined.

From the available information, the unit for classification should be cultivar/locality/year combinations and not the used area/year combination.

This approach offers a way to reduce nitrocellulose heterogeneity and produce a higher quality nitrocellulose.

In all characteristics measured second cut linters was superior to millrun in terms of homogeneity, means and distribution.

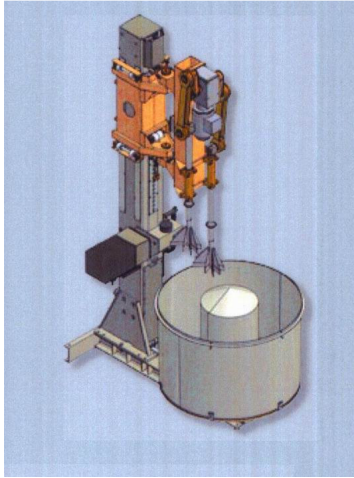
Results of this investigation confirmed that the change from millrun to second cut linters have improved the quality of all types of nitrocellulose manufactured.

2.3.2.3 Linter purification at the Wellington Site

Millrun and second cut linters were purified for many years at the Somerset West Site. The Millrun linters were utilized for double base rocket propellants. The Millrun linters gave better mechanical properties to rocket propellant grains than second cut linters. Second cut linters were utilized for small, medium and large caliber gun propellants.

A new linter purification plant was build and commissioned in 1984 at the Wellington Site. The new process consists of mechanical cleaning of the raw cotton linters, cake pressing, caustic extraction in pressure vessels (kiering), washing and bleaching, cake disintegration/shredding, washing, centrifuging, drying and baling.

Mainly second cut linters were purified at the new site. First cut on their own caused major plant operation problems. At some stages mixtures of second cut and first cut linters were purified but still some plant operation problems were encountered. In the end only second cut linters were purified and utilized.



Linters cake stamping press



Extraction and bleaching vessels



Extracted and bleached linters cakes



Linter cake opener

Pictures of equipment from web www.erbatech.de

Purification of South African ginned cotton linters continued until 2003. In 2003 Clark Cotton who for the previous decade supplied all second cut raw cotton to RDM announced that ginning operations of all linters would be terminated in South Africa from 2004 onwards. This implied that no second cut raw linters would be available in South Africa in future.

A feasibility study executed at that stage indicated that it would be more cost effective to import purified linters instead of raw cotton linters. By shipping raw linters about 23% trash is shipped as well. It is more cost effective to ship already purified linters. The decision was taken to mothball the linter purification plant. This necessitated the evaluation of overseas purified cotton linters from various purifiers.

The selection parameters were quality of samples together with delivery reliability and cost. It was decided to qualify second cut purified linters from the Buckeye Glückstadt, Germany plant. On discussions with Buckeye we could get linters that came from the same locality/region every year, which assisted in reducing the natural variation in linters. RDM got excellent service from Buckeye, Germany and all worrying concerns seemed to have been put aside.

The methodology that is followed to qualify a new linter supplier is as follows:

1. Supply Chain attains a linter tender sample (2 kg) together with a certificate of analysis from a specific supplier.
2. The RDM quality control laboratory analysis the sample in accordance to RDM's linter specification. Should there be differences in results between the supplier and RDM's laboratory the analytical test methods are aligned or calibrated.

3. When the tender sample passes the specification a trial container (18-20tons) is ordered for plant trial nitration runs.
4. On arrival of the trial container samples are analyzed to determine compliance to the specification and compare with suppliers certificate of analysis. The test results are submitted to the Material Revision Board that approves the release of the consignment for nitrocellulose manufacture.
5. The final test results of the nitrocellulose once again are submitted to the Material Revision Board for approval of the release of the nitrocellulose for the manufacture of specific propellants.
6. Propellant is manufactured and the performance of the nitrocellulose in the propellant process is monitored. The final propellant is tested for chemical composition, ballistic performance and shelf life. All the results are submitted to the Material Revision Board for release of the propellant for delivery to client or internal use in ammunition manufacture.
7. The Material Revision Board also declares the purified second cut linters from a specific supplier as being qualified.

Then unfortunately Buckeye USA took the decision to close the Glückstadt Germany plant. This closure would be effective from December 2005.

Other suppliers of purified cotton linters such as Milouban (Israel), Jinhanjiang (China), Xixiang T.N.C. Chemical Company (Taiwan) and Rudong Haiyu Fibre Company (China) were selected as possible suppliers. Only three of them are qualified suppliers at present.

RDM visits the purification plants and checks the purifier's quality and ISO systems.

At present RDM has to live with the situation that it has to accept the linter consignments by certificate of analysis and re-testing in-house. RDM has no control of which cotton growing area the raw cotton linters come from and what cultivars are being planted. Not the ginnery only the purifier is known to RDM.

One moved from a situation of being totally in control to a situation with many unknowns and uncertainties.

3. References

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