

GENERAL DYNAMICS

Ordnance and Tactical Systems—Canada Valleyfield



Characterization of the fiberization quality of nitrocellulose by elutriation

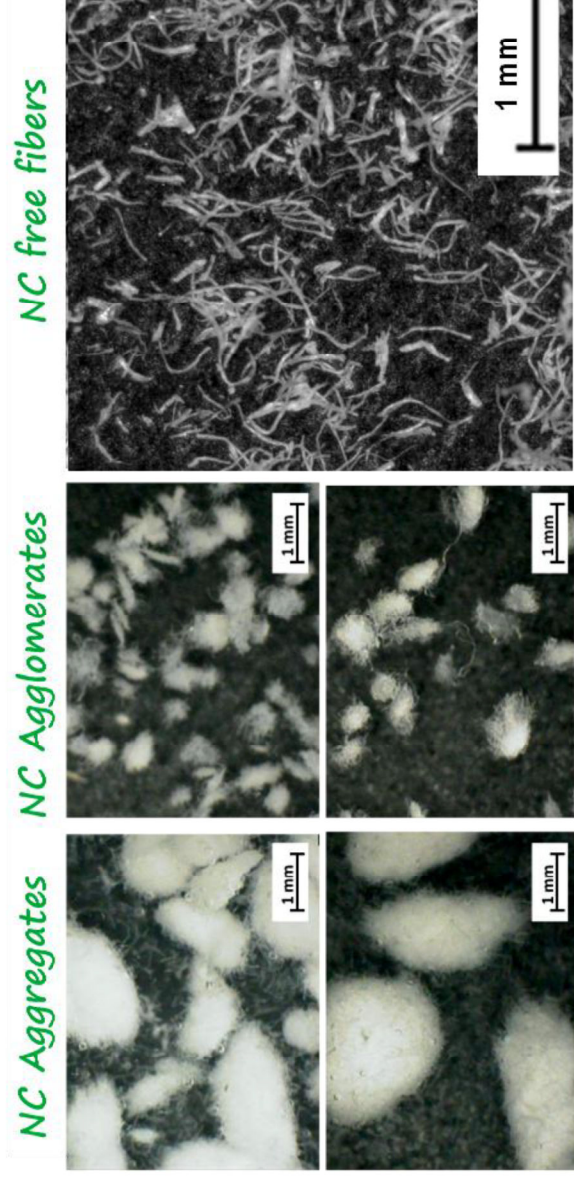
*6th International Nitrocellulose Symposium
23th-24th of April 2014
Hosted by TNO
Rijswijk, The Netherland*

Prepared by Mario Paquet and Ian Levac

Fiberization quality

NC is ideally composed of free fibers, the bulk of which fit the proper fiber length distribution. For numerous reasons, some NC fibers can be combined together to form larger pieces.

These pieces which are multi-fibre entities are basically of two types that can be defined by their mechanical resilience: the most resilient type are called agglomerates and the medium and low resilient types are called aggregates.



Fiberization quality

Agglomerates are:

- Fibers bound together in fiberboard and fused during nitration
- Requires very energetic process equipment for fiberization (refiners or deflakers)
- Produced from the original fiberboard or from fiber entanglements for baled cotton.

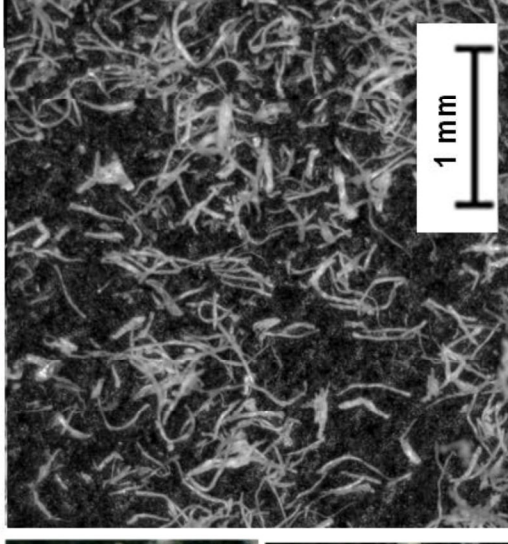
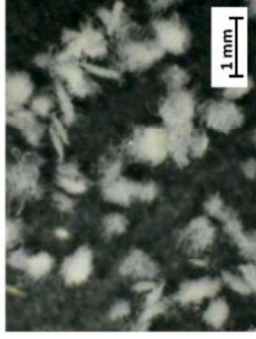
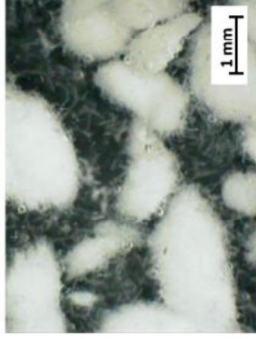
Aggregates **contrary to agglomerates**; are:

- Fibers bound together in dewatering centrifuge but not fused together
- Created only within the NC manufacturing process usually in the dewatering section

NC Aggregates

NC Agglomerates

NC free fibers



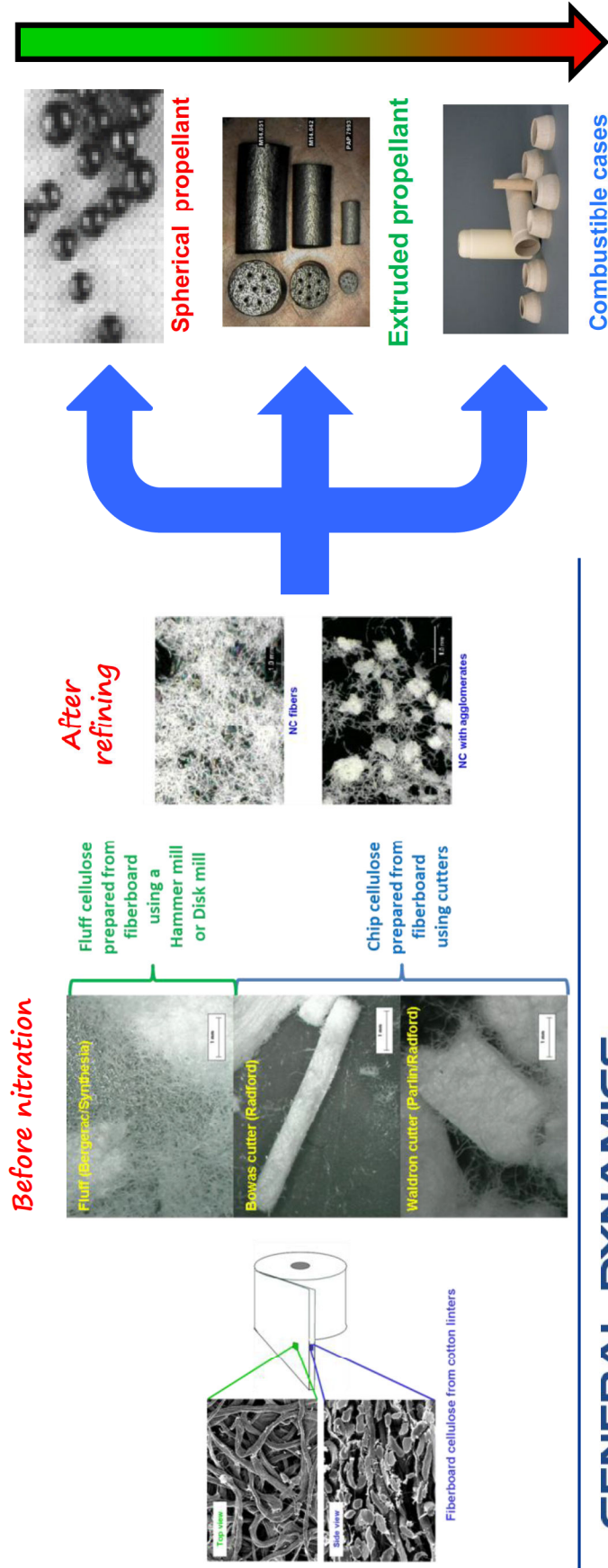
Aggregates are typically much larger (10X) than agglomerates

Fiberization quality

The tolerance for non-fiberized NC is application specific.

- At one extreme: spherical propellant applications are not significantly affected by the presence of non-fiberized NC
- At the other extreme: the combustible cartridge case applications can significantly be affected by the presence of non-fiberized NC
- Extruded propellant applications are in between the two extremes and tolerance to the presence of non-fiberized NC is very application specific.

*Tolerance
non-fiberized
NC*

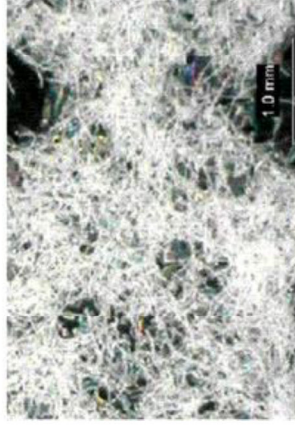


Fiberization quality



Extruded propellant

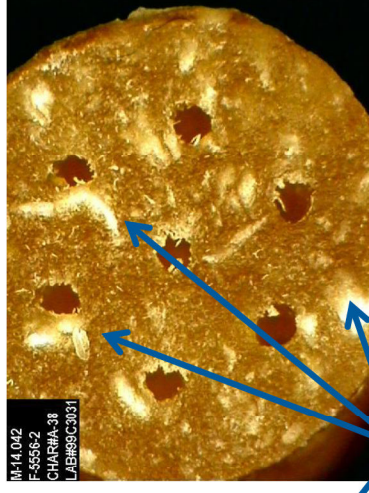
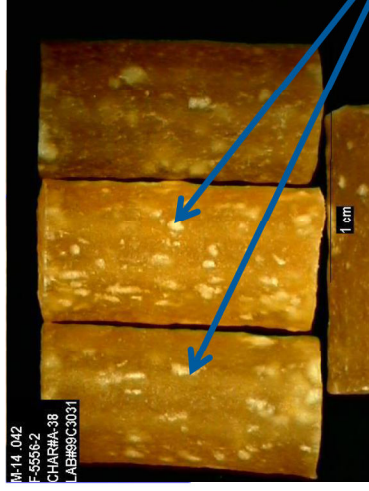
Large amounts of agglomerates in NC can affect the quality of some propellants, visual aspect and ballistic performance



NC fibers

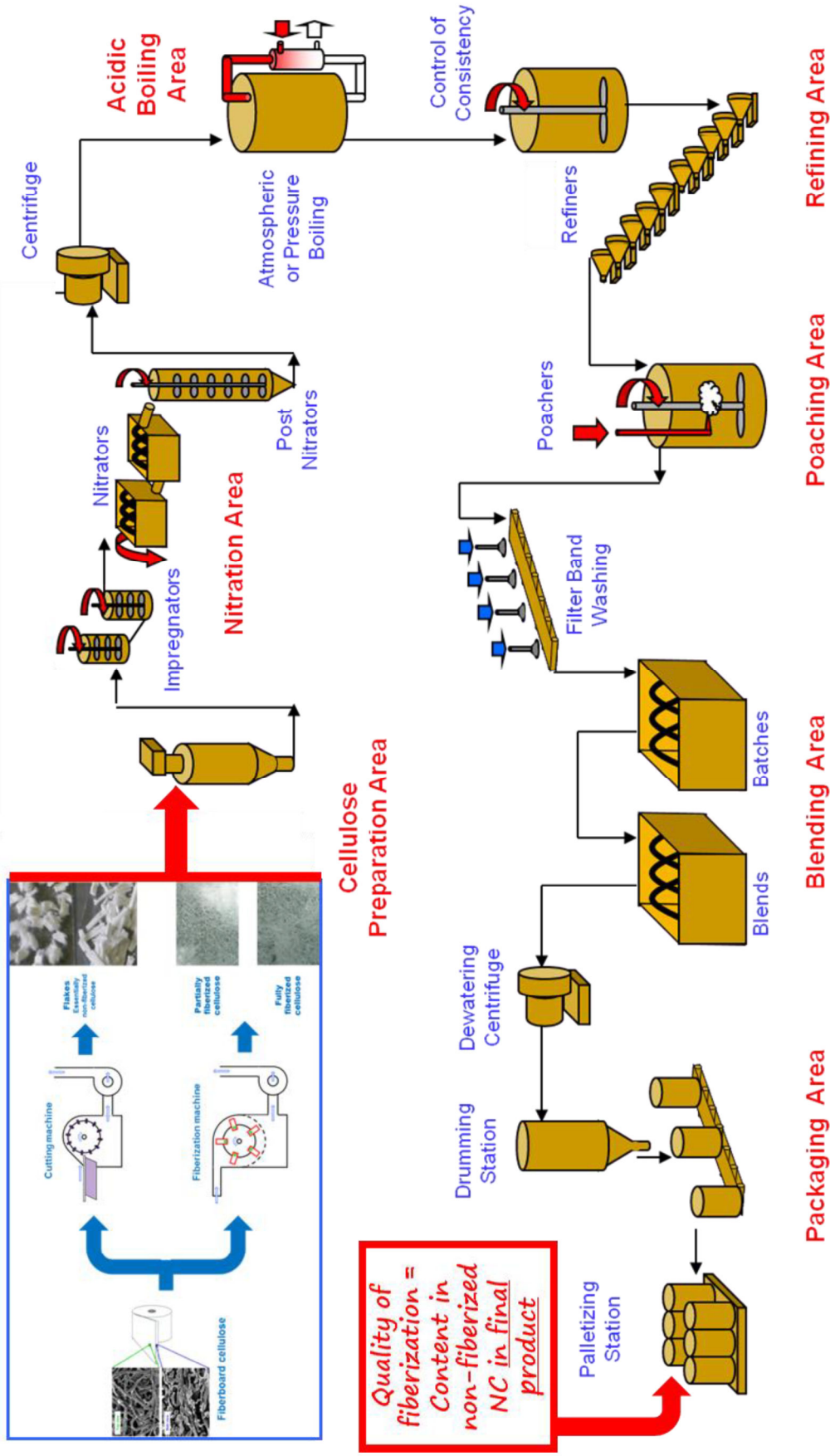


NC with agglomerates



Large pieces of uncolloided NC imbedded in the propellant matrix

Fiberization quality



The diagram illustrates the nitration process for cellulose, divided into several key areas:

- Cellulose Preparation Area:** This section shows the initial stages of cellulose processing. It includes a **Cutting machine** that produces **Flakes** (labeled as *Essentially non-fiberized cellulose*). These flakes are then processed by a **Fiberization machine** to create **Partially fiberized cellulose** and finally **Fully fiberized cellulose**. A **Fiberboard cellulose** sample is also shown. A red arrow indicates the flow from the cutting machine to the fiberization machine.
- Nitration Area:** This central area is where the cellulose is nitrated. It includes **Impregnators**, **Nitrators**, and **Post Nitrators**. A red arrow points from the cellulose preparation area to the impregnators. A green arrow points from the post nitrators to the refining stage. A red arrow points from the post nitrators to the dewatering centrifuge.
- Acidic Boiling Area:** This area includes a **Centrifuge** and a **Boiling tank** (labeled **Atmospheric or Pressure Boiling**). A red arrow points from the post nitrators to the boiling tank. A green arrow points from the boiling tank to the refining stage.
- Refining and Washing:** This section includes **Refiners**, **Poachers**, and **Filter Band Washing**. A green arrow points from the boiling tank to the refiners. A red arrow points from the poachers to the filter band washing.
- Aggregates and Blends:** This area shows the formation of **Aggregates** (labeled *Aggregates formed here by compression of free fibers*) and **Blends**. A red arrow points from the filter band washing to the aggregates. A green arrow points from the aggregates to the dewatering centrifuge.
- Final Processing:** This section includes a **Dewatering Centrifuge**, a **Drumming Station**, a **Palletizing Station**, and a **Palletizing Station**. A red arrow points from the dewatering centrifuge to the drumming station. A green arrow points from the drumming station to the palletizing station. A red arrow points from the palletizing station to the final product.

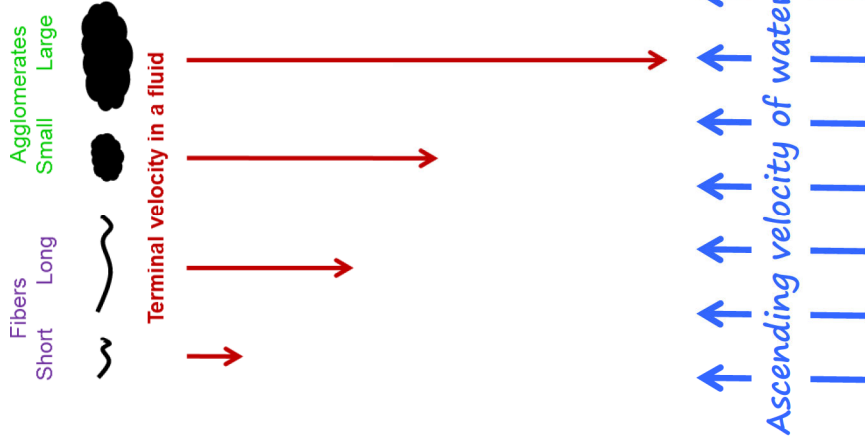
A red box at the bottom left contains the text: **Quality of fiberization = Content in non-fiberized NC in final product**.

Packaging Area

Description of cone elutriator

5th International Nitrocellulose Symposium
Spiez, Switzerland; April 17-18, 2012

Fiberization quality quantification:
Elutriation method using a
modified Imhoff sedimentation cone



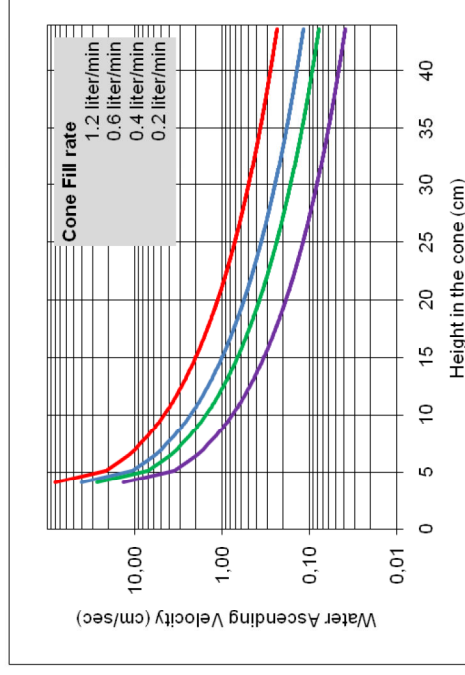
A basic elutriator follows these basic principles:

- different masses and shape have different terminal velocity when falling in a fluid
- creating an ascending velocity gradient with high velocity in the bottom and low velocity on the top can produce a simple mean of achieving physical separation and quantification

Since the ascending velocity of water flow is in a cone: a velocity gradient is established

The ejection velocity is the ascending velocity at the top of the cone where ejection is taking place

Any particle with a falling velocity smaller than the ejection velocity will be ejected from the elutriator



Separating sinkers and floaters by elutriation

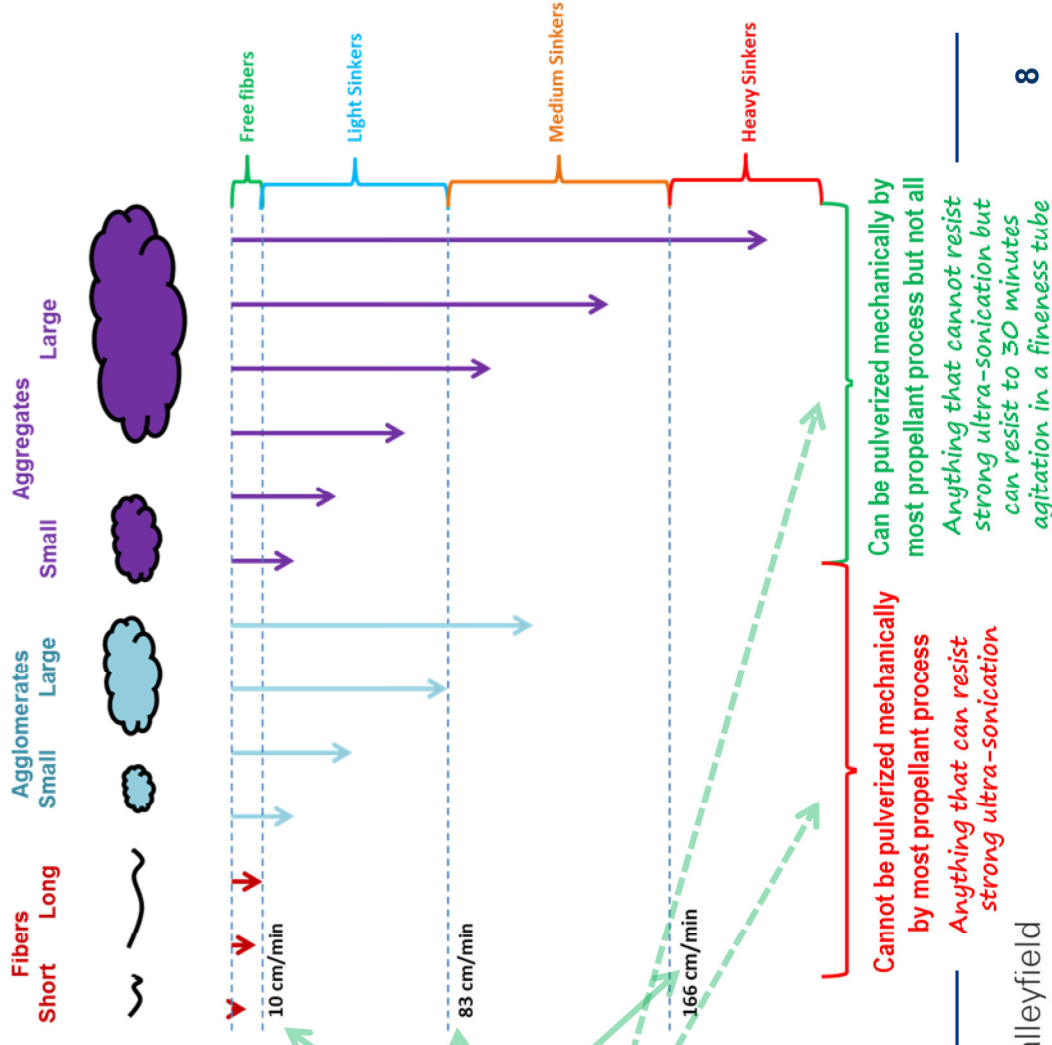
Terminal velocity in water of NC Free fibers/Agglomerates/Aggregates

The ejection velocities are arbitrary and can be modified. However in general, the ejection velocity is selected to correspond to the terminal ascending velocity of the most common types of non-fiberized NC.

One, must establish 2 things from the start:

- the sinkers size that can be tolerated by the propellant process
- the mechanical resilience threshold that can be tolerated by the propellant process

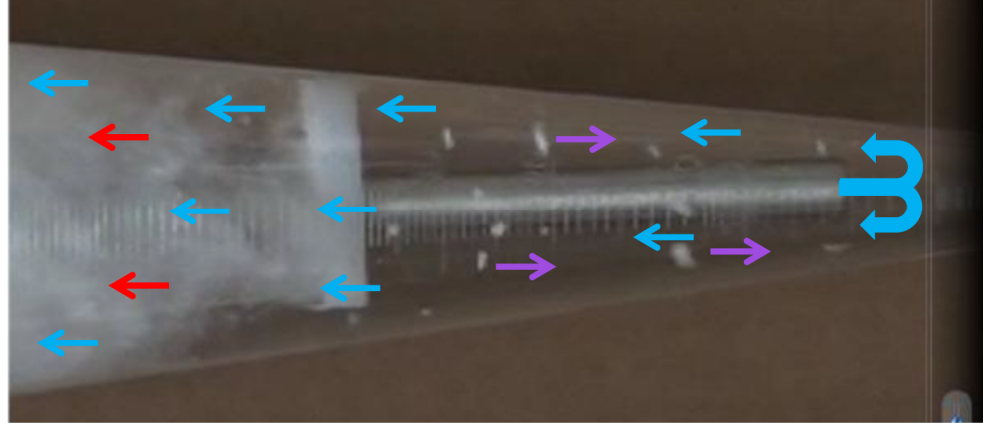
The values listed by the Mil-DTL are specific for North American propellant processes.



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Elutriation assembly



In the end, only pieces of NC are left for quantification

Sample 1
Grade A
Cotton
Fiberboard/Cutter
Gravimetric 22.9%
Volumetric 11 ml



Sample 2
Grade B
Cotton
Fiberboard / Cutter
Gravimetric 0.82%
Volumetric 0.45 ml

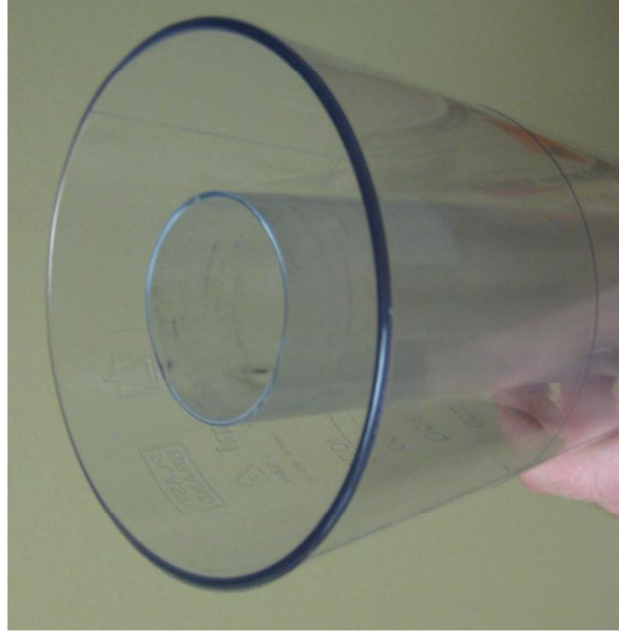
Sample 3
Grade A
Cotton
Fiberboard / Hammer
Gravimetric 0.23%
Volumetric 0.25 ml



Sample 4
Grade A
Cotton
Fiberboard / Hammer
Gravimetric 0.04%
Volumetric 0.05 ml

An ascending flow of water carry away the free fiber NC while heavier pieces of NC sink in the cone

Elutriation assembly



A multi-cone assembly was constructed to analyse several samples concurrently.

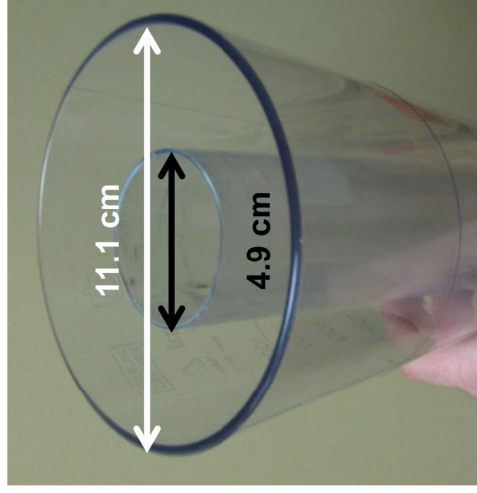
The straight section is added to the cone to reduce water consumption at high ejection flow rate and to limit turbulence in the lower section of the cone.

Elutriation assembly

The terminal ascending velocity of the elutriator is adjusted using the flowrate of water
The following relation provides the ascending velocity:

$$\text{Water ascending velocity (cm/min)} = \text{Flow rate (cm}^3\text{/min)} / \text{Area outlet (cm}^2\text{)}$$

Ejection velocity cm/min	Diameter of outlet cm	Water flowrate ml/min	Nominal flow rate ml/min
10	11.1	968	950
83	11.1	8032	
166	11.1	16064	
83	4.9	1565	1500
166	4.9	3130	3000



Using the set-up presented at the 5th NC symposium, an ejection velocity of 166 cm/min would requires a flow-rate of 16 liters/min. In order to reduce the water consumption and improve separation at higher velocity a straight column of reduced diameter (4.9cm) is added to the elutriator.

This reduces the flow rates for fast ejection velocities by a factor of 5.

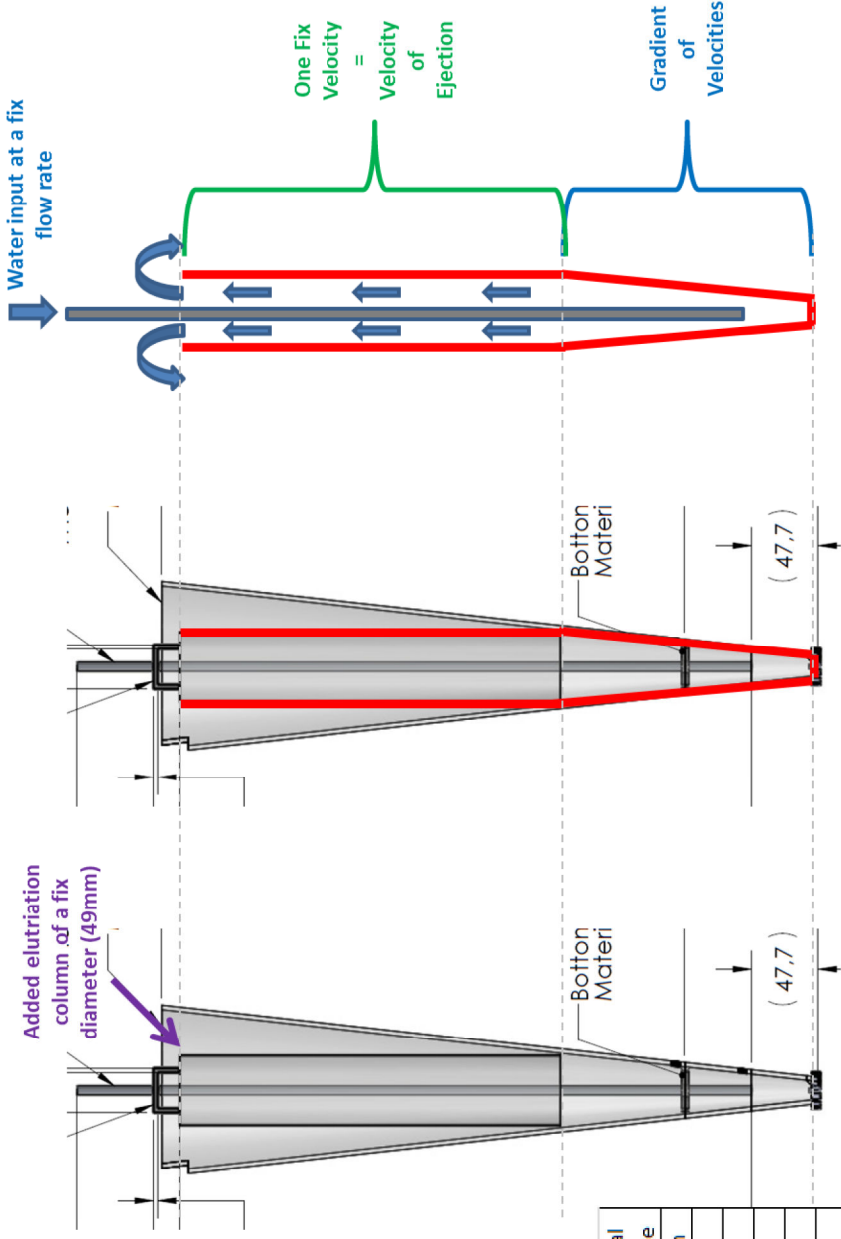
Elutriation assembly

Addition of an elutriator column to the cone to produce an enhance classification at a fix Ejection Velocity

Schematics of the equipment are available

Parts and/or full set-up (single or multi-cone) are also available

A training video is available to guide installation and operation of the equipment



Ejection velocity cm/min	Diameter of outlet cm	Water flowrate ml/min	Nominal flow rate ml/min
10	11.1	968	950
83	11.1	8032	
166	11.1	16064	
83	4.9	1565	1500
166	4.9	3130	3000

Elutriation method for quantification of quality of fiberization

This test is based on the following principles:

- free fibers have terminal falling velocities less than about 10 cm/min (equivalent to a flow rate of 950 ml/minutes in the standard cone elutriator -height of 43.3 cm, diameter 11.1 cm)
- agglomerates and aggregates have terminal falling velocities greater than about 10 cm/min
- agglomerates are strong enough to resist long periods of strong ultra-sonication (15 minutes)
- aggregates do not resist any exposure to ultra-sonication but can resist mechanical agitation equivalent to mixing in 200 ml of water in a fineness tube rotated end over end at a rate of 12 rotation/minutes for 30 minutes.

Elutriation method for quantification of quality of fiberization

Minimum time required for adequate classification

Weight of NC 15 g

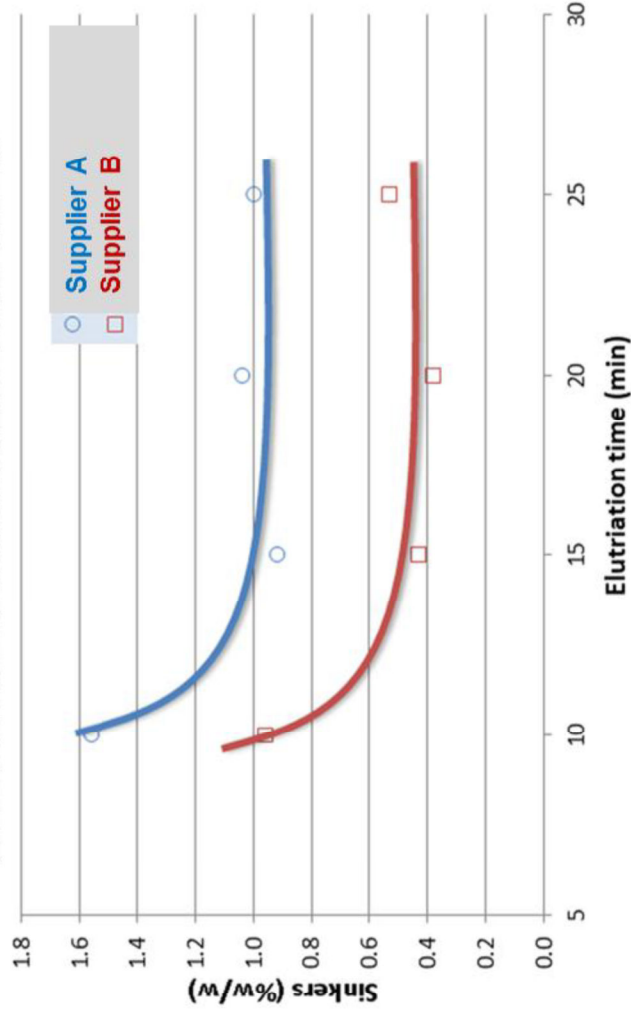
Mixing @12rpm for 30 minutes

Pre-elutriation for removal of free fibers: 15 minutes flowrate of @950 ml/min

Cone with elutriation column using a flow rate of 3000 ml/min

Elutriation time with elutriation column minutes	Supplier B		Supplier A	
	% sinkers	100	% sinkers	100
0				
10	1.56		0.96	
15	0.92		0.43	
20	1.04		0.38	
25	1.00		0.53	

Content in Sinkers relative to elutriation time



Elutriation method for quantification of quality of fiberization

After assisting many lab introducing this method, it was found that many lab technicians do not understand ultra-sonication although most labs are equipped with it.

The most common equipment is an ultra-sonication bath which can contain several liters of water because the bath is often also a thermostatic bath.

Ultra-sonication requires a liquid to carry the sonication wave. Although a certain quantity of water is necessary to carry the sonication wave, the ultra-sonication energy transmitted to the sample is inversely proportional to the water content in the bath (the more water added to the bath, the lower the ultra-sonication effect). This includes the water in the beaker that goes into the bath: both must contain a minimum amount of water.

The discomforting sound made by the ultra-sonication is a good sign that the ultra-sonication is doing its work: adding water to the bath reduces the frequency of the sound and makes it more comfortable to the lab environment however the sonication is rendered useless.

Therefore the ultra-sonication conditions must be standardized so the method is clear and the effect achieved.

Elutriation method for quantification of quality of fiberization

The following variables are important to obtain reproducible results:

- the amount of water in the fineness tube (200ml)
- the use of a standard container for mixing (the fineness tube)
- the mixing time (30 minutes)
- the rate of rotation (12 rotation/minutes)
- the mode of rotation (end over end)
- the use of water wet NC
- the moisture content of the wet NC (for 2 reasons): One, the test becomes meaningless for aggregates if NC is dried. Second, the moisture content is important to calculate the exact amount of NC wet required to have 4.0 g (or 15g depending on the test) of NC equivalent dry.
- the quality of the water for the elutriation

Elutriation method for quantification of quality of fiberization

The complete set of analysis available is the following:

Total Sinkers
Total Agglomerates
Total Aggregates

= Content in Sinkers @ 10 cm/min
= Content in Agglomerates @ 10 cm/min
= Total Sinkers – Total Agglomerates

Heavy Sinkers
Heavy Agglomerates
Heavy Aggregates

= Content in Sinkers @ 166 cm/min
= Content in Agglomerates @ 166 cm/min
= Heavy Sinkers – Heavy Agglomerates

Medium Sinkers

= Content in Sinkers @ 83 cm/min - Content in Sinkers @ 166 cm/min
Medium Agglomerates = Content in Agglomerates @ 83 cm/min - Content in Agglomerates @ 166 cm/min
Medium Aggregates = Medium Sinkers – Medium Agglomerates

Light Sinkers

= Content in Sinkers @ 10 cm/min - Content in Sinkers @ 83 cm/min
Light Agglomerates = Content in Agglomerates @ 10 cm/min - Content in Agglomerates @ 83 cm/min
Light Aggregates = Light Sinkers – Light Agglomerates

Elutriation method for quantification of quality of fiberization

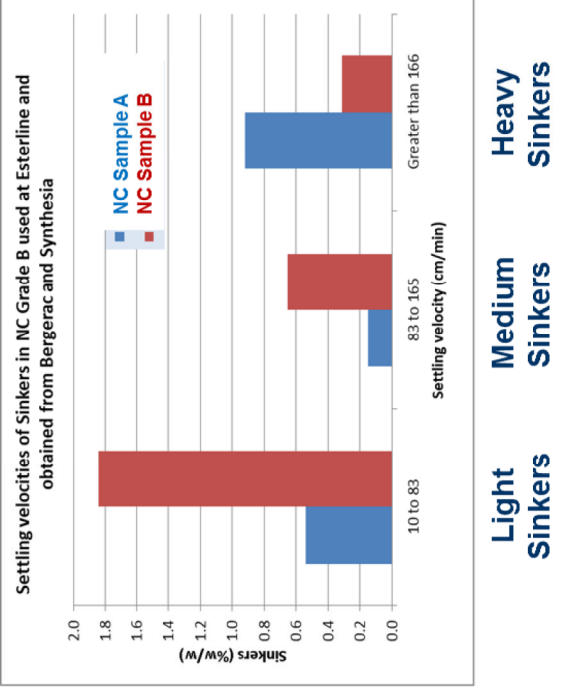
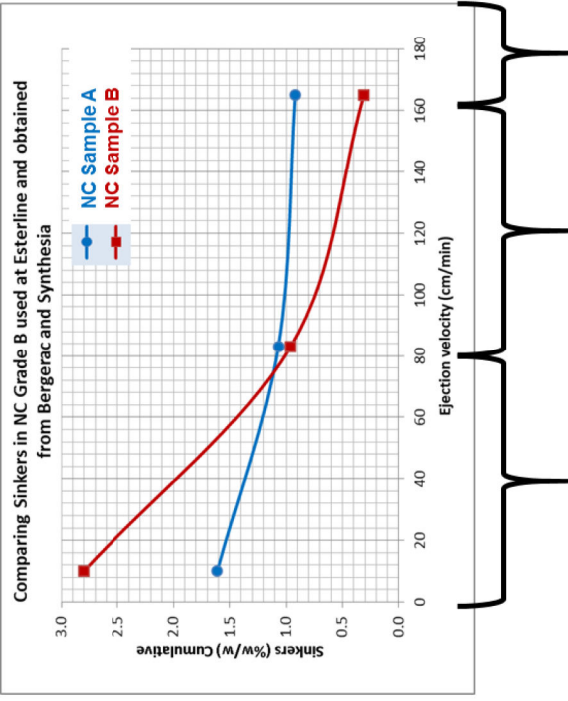


Separation by resilience

Separation by falling velocity

Grade	% Agglomerat > 10 cm/min	% Aggregat > 10 cm/min	% Total Sinkers	%Sinkers Light 10 to 83 cm/min	%Sinkers Medium 83 to 166 cm/min	%Sinkers Heavy > 166 cm/min
B	0.06	1.55	1.61	0.54	0.20	0.87
B	0.12	2.68	2.80	1.84	0.65	0.31

6 ejection velocities were tested, it was later reduced to 3 standard velocities.
Most often 1 or 2 is enough.



Elutriation method for quantification of quality of fiberization

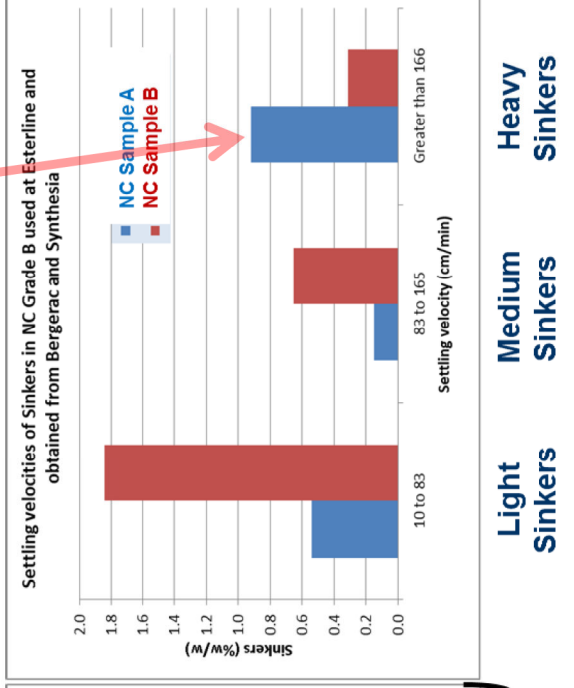
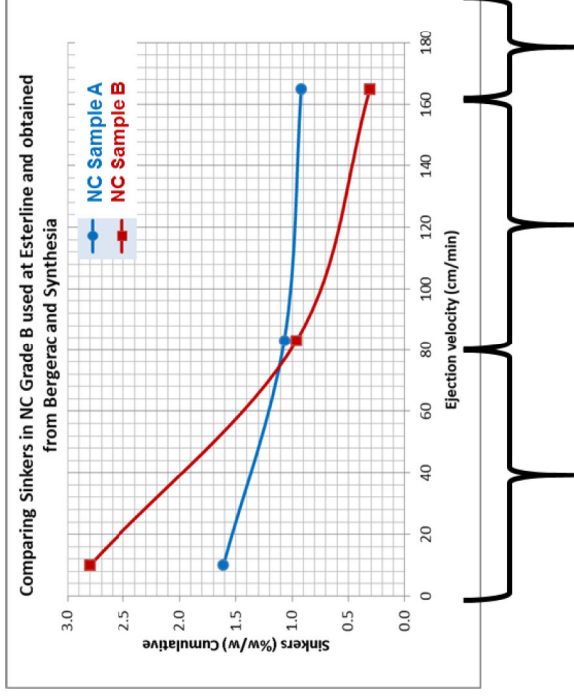


Separation by resilience

Separation by falling velocity

Grade	% Agglomerat > 10 cm/min	% Aggregat > 10 cm/min	% Total Sinkers	%Sinkers Light 10 to 83 cm/min	%Sinkers Medium 83 to 166 cm/min	%Sinkers Heavy > 166 cm/min
B	0.06	1.55	1.61	0.54	0.20	0.87
B	0.12	2.68	2.80	1.84	0.65	0.31

The data reveals that the NC sample A is affected negatively by the dewatering centrifuges and that the cellulose preparation and refining section are operating adequately.



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Summary of test conditions for fiberization quality

Main methods:

	Weight of NC (equivalent dry weight)		Volume of water		Mixing time at 12 rotation /min		First cone elutriation time		Flow rate		Settling time		Number of beaker wash		Volume of water for ultra-sonication		Time for ultra-sonication		Number of beaker wash		Quantification by filtration with fritted glass crucible	
	g	ml	minutes	minutes	ml/min	minutes	ml/min	minutes	minutes	ml	minutes	ml	minutes	ml	minutes	ml	minutes	ml	minutes	ml	minutes	
Content in Sinkers @ 10 cm/min																						
Content in agglomerates @ 10 cm/min	4	200	30	15	950	5	3													Yes	Yes	
Transfer content of crucible with Sinkers @10cm/min in a beaker																						

Secondary methods:

	Weight of NC (equivalent dry weight)		Volume of water		Mixing time at 12 rotation /min		First cone elutriation time		Flow rate		Settling time		Second cone elutriation time		Using straight section		Settling time		Quantification by filtration with fritted glass crucible	
	g	ml	minutes	minutes	ml/min	ml/min	minutes	minutes	minutes	minutes	minutes	minutes	ml/min	ml/min	minutes	minutes	minutes	minutes		
Content in sinkers @ 83 cm/min	15	200	30	10	950	3	10						1500	2				Yes		
Content in sinkers @ 166 cm/min	15	200	30	10	950	3	10						3000	2				Yes		

Fiberization quality of NC relative to final applications

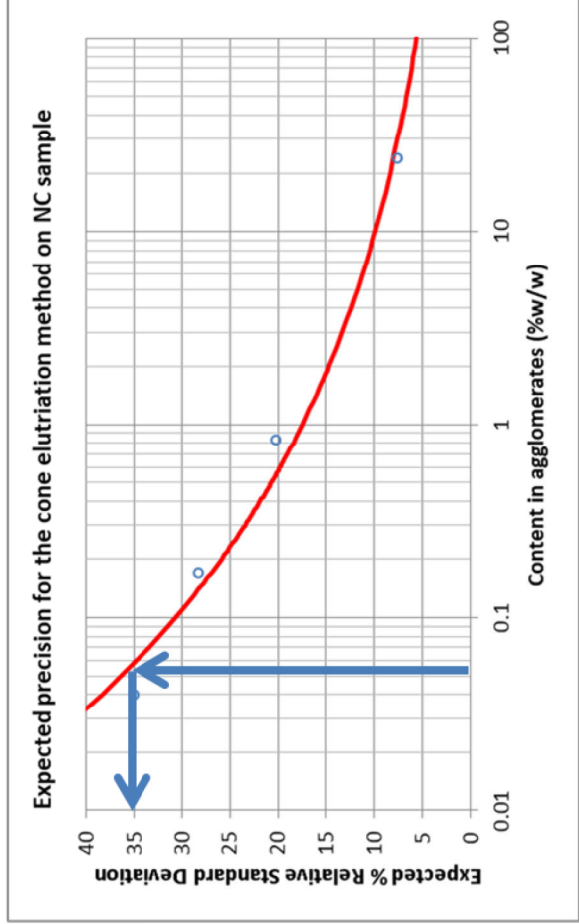
The fiberization quality of NC can be segmented in the following manner:

Agglomerate content in NC				
Combustible Cartridge Case	Extruded propellant	Spherical propellant	Less than	
X	X	X	0.25	
X	X	X	0.5	
	X	X	1	
	X	X	5	
	X	X	20	
	X	X	50	
		X	100	
		Aggregate content in NC		
		Combustible Cartridge Case	Less than	
The fiberization quality is an order of magnitude test. For example, nothing magic happens between 4.9 and 5.1%.		X	0.75	
		X	1.0	

Elutriation method for quantification of quality of fiberization

Data obtained on a Reproducibility and Repeatability test

The main data was presented at the *5th International Nitrocellulose Symposium in Spiez, Switzerland*; but did not include the lasted method improvements/modifications



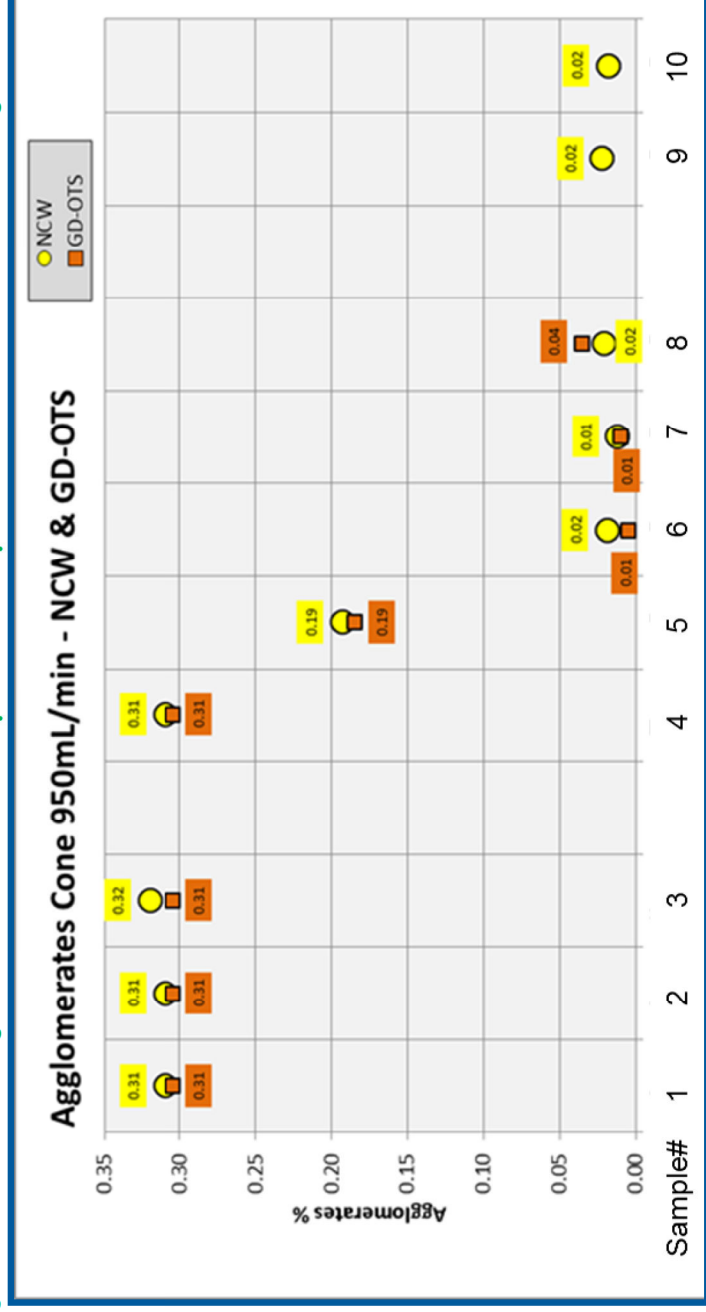
Lot	Drum	Technician	Repeat #	% Agglomerat	% Total Sinkers	%Sinkers Light 10 to 83 cm/min	%Sinkers Medium 83 to 166 cm/min	%Sinkers Heavy > 166 cm/min
1	2	1	1	1.27	0.26	1.53	1.51	0.00
			2	1.11	0.25	1.36	1.31	0.00
			3	1.19	0.44	1.63	1.60	0.00
			Average	1.19	0.32	1.51	1.47	0.00
			1	1.22	0.29	1.51	1.50	0.00
	19	1	2	1.13	0.27	1.40	1.38	0.00
			Average	1.18	0.28	1.46	1.44	0.00
			1	1.03	0.20	1.23	1.19	0.00
			2	1.04	0.25	1.29	1.26	0.00
			3	1.24	0.34	1.58	1.55	0.00
2	3	1	Average	1.10	0.26	1.37	1.34	0.00
			1	0.33	0.95	1.28	0.94	0.10
			2	0.28	0.92	1.20	0.97	0.09
			3	0.19	1.16	1.35	1.00	0.16
			Average	0.27	1.01	1.28	0.97	0.12
	19	1	1	0.24	1.61	1.85	1.35	0.11
			2	0.20	1.75	1.95	1.61	0.09
			3	0.16	1.29	1.45	1.01	0.35
			Average	0.20	1.55	1.75	1.33	0.30
			1	0.03	0.12	0.15	0.07	0.03
3	34	1	2	0.04	0.17	0.21	0.14	0.06
			3	0.07	0.14	0.21	0.11	0.06
			Average	0.05	0.14	0.19	0.11	0.06
			1	0.07	0.16	0.23	0.12	0.05
			2	0.08	0.17	0.25	0.21	0.03
	49	1	Average	0.08	0.17	0.24	0.17	0.04
			1	0.05	0.28	0.33	0.00	0.21
			2	0.05	0.43	0.48	0.00	0.29
			3	0.12	0.19	0.31	0.00	0.17
			Average	0.07	0.30	0.37	0.00	0.22
4	4	1	1	0.03	0.26	0.29	0.00	0.41
			2	0.01	0.42	0.43	0.00	0.27
			3	0.03	0.24	0.27	0.00	0.34
			Average	0.02	0.31	0.33	0.00	0.34
			1	0.03	0.37	0.40	0.00	0.19
	18	2	2	0.05	0.37	0.42	0.02	0.18
			Average	0.04	0.37	0.41	0.01	0.19
			1	0.04	0.37	0.42	0.02	0.18
			2	0.05	0.37	0.42	0.02	0.18
			Average	0.04	0.37	0.41	0.01	0.19

Elutriation method for quantification of quality of fiberization

Inter –lab testing:

Testing made by GD-Valleyfield and NitroChemie Wimmis on samples provided by NitroChemie Wimmis are in good agreement.

It took concerted effort to train lab technicians for this test. Success was achieved only after exchange of known samples and production of a training video.



Quantification of quality of fiberization

In summary:

- This test is designed to provide quantitative information about the non-fiberized NC present in final product but can also be used to guide refining process.
- It will not work on NC prior to refining because of excessive fiber length.
- It will be included in the next revision of the Mil-DTL-286 and is already used in acquiring NC for various applications.

