9th International Nitrocellulose Symposium

Preparation and properties of energetic nitrocellulose from pulverized cellulose

North Chemical Industries Co., Ltd in China

Hong Yang, Qinghai Qiu, Renxu Zhang

June 2023 Birmingham,UK

CONTENTS

01 Introduction

02 Method of PNC preparation

03 Results and Discussion

04 Conclusion

05 Prospects

1 Introduction

1.1 Introduction of energetic nitrocellulose

Energetic nitrocellulose (NC for short) is the basic energetic material for gun propellants, solid rock propellants, combustible cartridge case and so on.

Contain more than 95% of NC

Single-base Gun Propellant

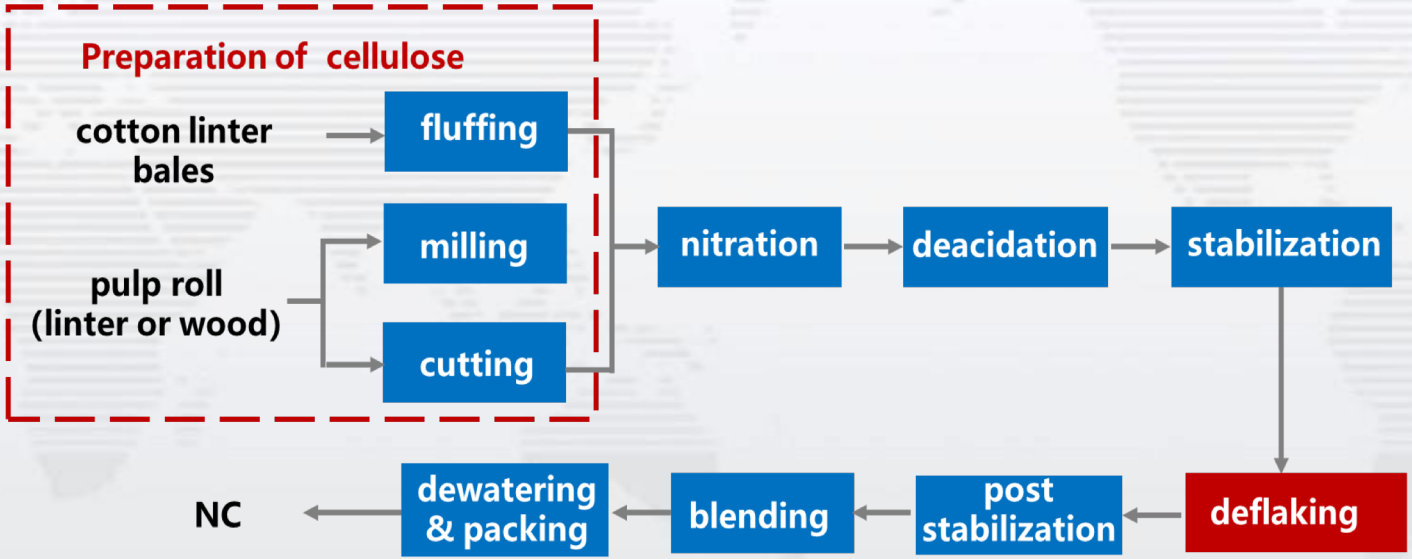
Contain more than 50% of NC

Double-base Gun Propellant

1 Introduction

1.2 Traditional method for NC preperation

- Traditional NC is produced from cotton linter bales to be fluffed, cotton or wood pulp rolls to be milled or cut,the process flow is as follows.



- The deflaking process is highly energy-intensive, accounting for **over 50% energy consumption** of the NC producing.

The advantages and disadvantages of the fluffed cotton linter for NC producing

cotton linter bales

Fluffed

Advantages:

1.high reactive activity

2. high content of α-cellulose

3.high yield of NC

Disadvantages:

1. Lower concentration in the slurry result in high water consumption for material transportation;

3. low utilization rate of equipment;

4. continuous operation is difficult ;

1 Introduction

The advantage and disadvantages of shreds cellulose

linter/wood Pulp roll

milled

Shreds

Advantage

1. the high reactive activity is similar to cotton linter ;

Disadvantages

1. nonuniform particle size;
2. high acid to cellulose ratio;
3. low yield;

1 Introduction

The advantage and disadvantages of chips cellulose

Linter/wood pulp roll

cut

Chips

Disadvantages

1. high requirement of equipment
2. long nitration time, high nitration temperature and high nitric acid content

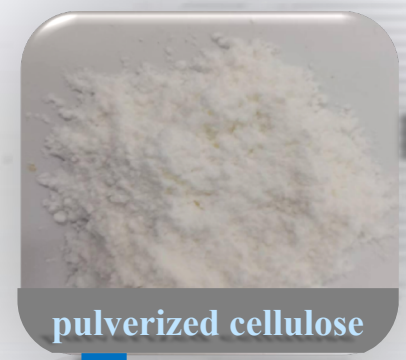
Advantage

1. low acid to cellulose ratio

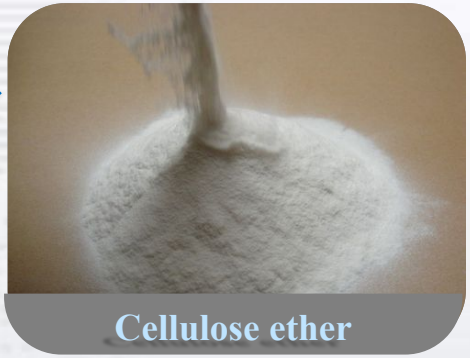
1 Introduction

Application of pulverized cellulose

- Pulverized cellulose is using for cellulose ether producing.



Etherified

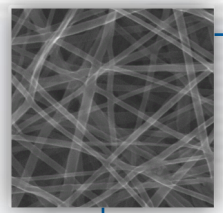


Nitrated

- So can we just use pulverized cellulose to produce NC directly and then eliminate the deflaking process?

1 Introduction

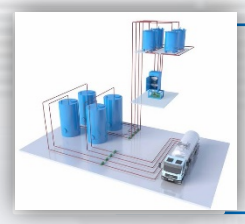
Why did we choose pulverized cellulose to prepare NC?



- The huge surface area of pulverized cellulose help to enhancing the quality of the nitration;

- The cellulose particle size is small;

  So could we eliminate the deflaking process to simplify NC producing flow and save energy?

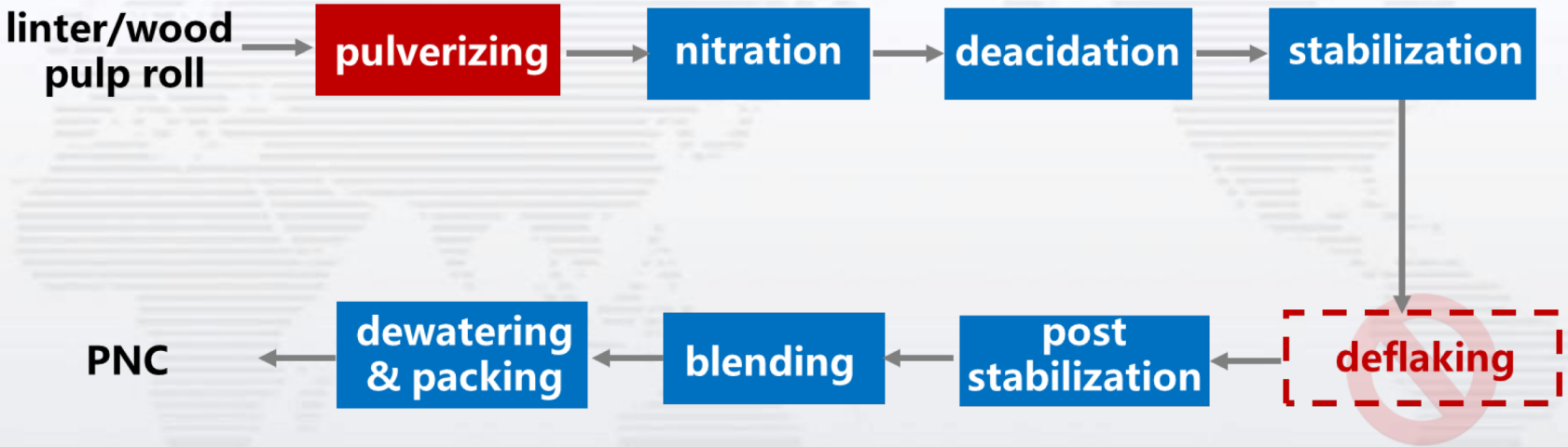


- The higher materials content in slurry resulted in lower acid and water consumption. we also can increase material content in equipment to obtain higher equipment efficiency.

- For those, we have studied on the preparation of **PNC** (NC prepared using pulverized cellulose). Then we'll discuss the difference between PNC and **LNC** (NC **p**repared using cotton linter).

2 Preparation method

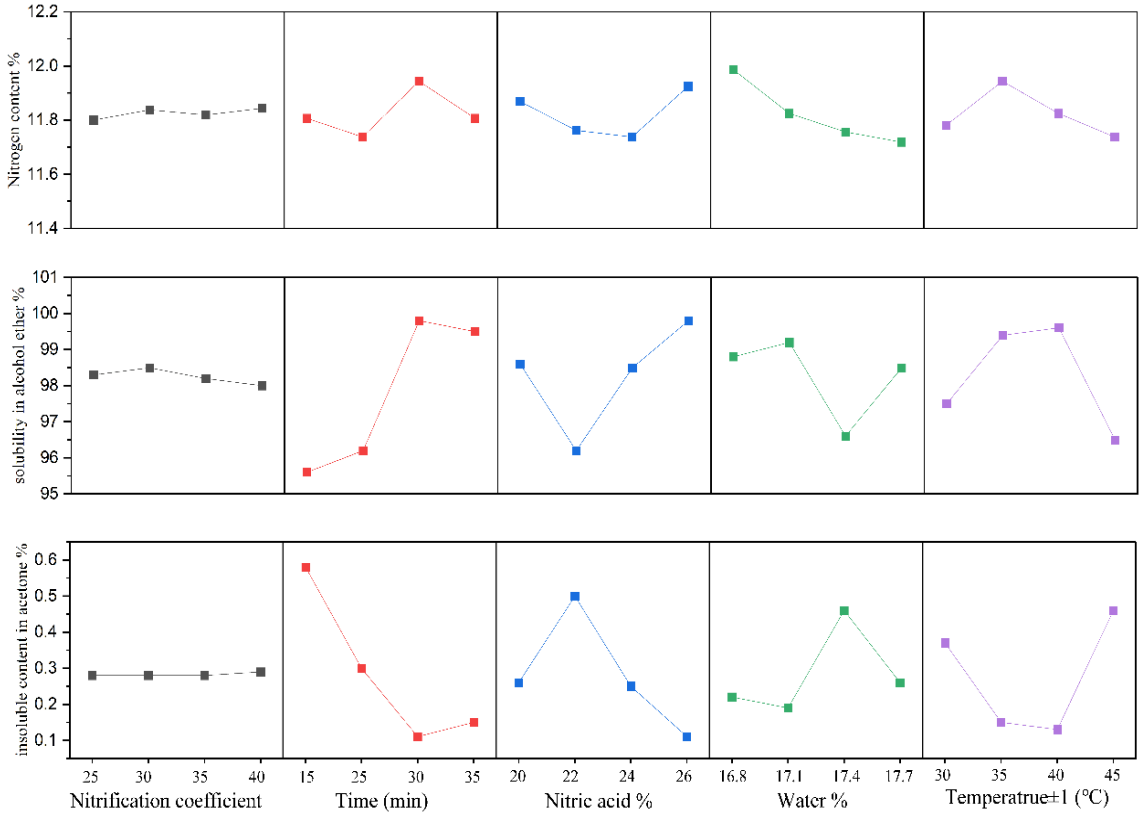
The process flow diagram of PNC is shown below :



- The pulverizing process replaces the cellulose preparation process, at the same time the deflaking process was eliminated .

3 Results and Discussion

Orthogonal experimental of pulverized cellulose's nitration



- When preparing PNC, we investigated orthogonal experimental of pulverized cellulose's nitration.
- The result is shown in the picture.

3 Results and Discussion

Orthogonal experimental of pulverized cellulose ‘s nitration

The effect on alcohol-ether solubility and insoluble substance in acetone from high to low

nitration time > nitric acid content in mixed acid > nitration temperature > acid to cellulose ratio

The effect on nitrogen content from high to low

moisture in mixed acid > nitration time > nitration temperature > acid to cellulose ratio

3 Results and Discussion

Comparison of nitration conditions among four types of cellulose

Materials	Nitrating Mixture %		Time min	Temperature ℃	Acid / cellulose
	nitric acid	water			
cotton linter	17~25	7~18	30~40	30~40	40~60
cotton or wood pulp(shreds)	20~30	7~19	20~30	40~50	70~100
cotton or wood pulp(chips)	45-55	7-19	60-90	45-55	18-22
pulverized cellulose	**17~25**	**7~18**	**25~35**	**30~40**	**25~35**

From the table above， pulverized cellulose's nitration is ：

1. lower nitric acid content in the mixed acid;
2. shorter nitration time;
3. lower nitration temperature ;

4. lower acid to cellulose ratio;

So the nitration reactivity is similar to cotton linter;

3 Results and Discussion

Properties of PNC

item		Nitrogen content%	Solubility in ethanol and ether%	Viscosit ymm²/s	Fineness ml	Stability NOml/g	Ash loss%	Alkalinity %	Insoluble substance in acetone %
NC with high nitrogen	PNC	**13.46**	—	**32.1**	**66**	**2.01**	**0.13**	**0.04**	**0.10**
	MIL-DTL-244C	≥13.20	—	by contr act	by contr act	≤2.5	—	—	≤0.4
	ČOS 137605	13.3 ~ 13.6	excellent ≤5.0	by contr act	80 ~ 140	1.5 ~ 2.5	0.15 ~ 0.45	0.02 ~ 0.15	Excellent ≤0.05
NC with low nitrogen	PNC	**12.16**	**99.7**	**38.6**	**68**	**1.45**	**0.12**	**0.03**	**0.10**
	MIL-DTL-244C	12.20 ±0.10	—	by contr act	by contr act	≤2.5	—	—	≤0.4
	ČOS 137605	11.8 ~ 12.8	excellent≥ 99.3	by contr act	by contr act	1.5 ~ 2.5	0.15 ~ 0.45	0.02 ~ 0.15	excellent ≤0.15

For standard

- The technology specifications of PNC besids fineness perfectly meet the technical requirements of ČOS 137605 and MIL-DTL-244C.

Eliminating the deflaking process is feasible in the PNC's preparation.

- PNC with high nitrogen is close to the excellent level of insoluble substance in acetone .
- PNC with low nitrogen has reached the excellent level of insoluble substance in acetone and solubility in ethanol and ether.

Measurement of PNC's fiber quality by Valmet Fiber Image Analyzer

Measurements	PNC			
	High nitrogen content		Low nitrogen content	
	PNC	LNC	PNC	LNC
Arithmetic mean fiber length of the range0.1~10.0 mm	**0.271**	0.234	**0.243**	0.167
Fiber width (length-weighted) , um	23.40	26.11	25.12	31.18
Class A fine fibers , %	**34.34**	47.95	**38.23**	77.47
Class B fine fibers , %	**1.03**	0.58	**0.08**	0.36
Fine fibers , %	70.97	83.02	71.99	93.30
Broom rate , %	0.29	0.28	0.30	0.42
Curl (length-weighted) , %	17.85	8.75	16.75	6.09

Results

1. The average length of PNC sample's fibers is relatively longer, with smaller average width and optical roughness than LNC's ;
2. PNC sample has less small fibers and higher curling than LNC's.

3 Results and Discussion

SEM image of LNC and PNC samples

LNC sample

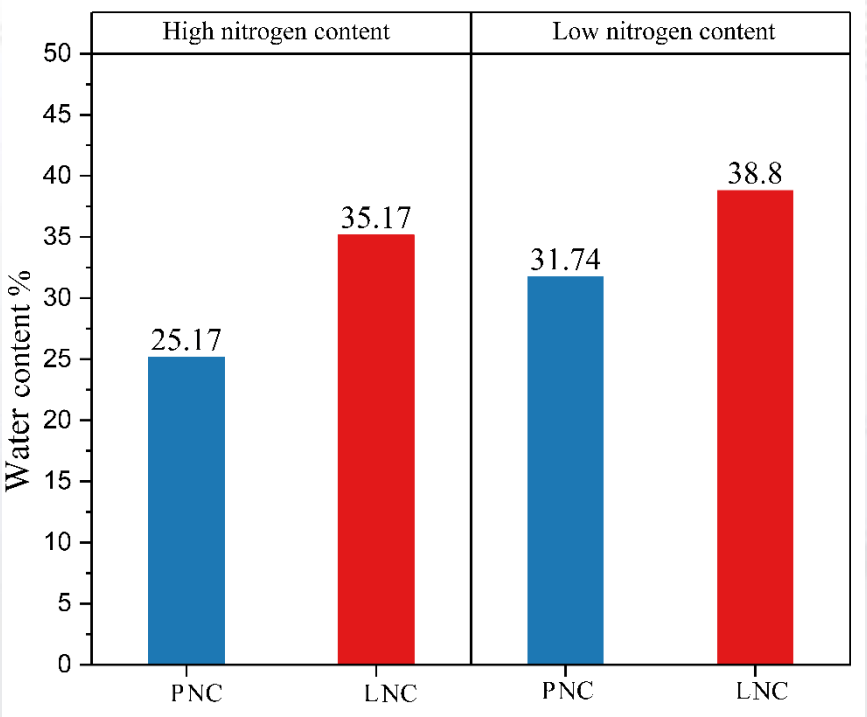
PNC sample

Results

1. It can be seen that the PNC sample retains a better fibrous tubular structure;
2. The structures of the LNC sample were severely damaged after deflaking process.

3 Results and Discussion

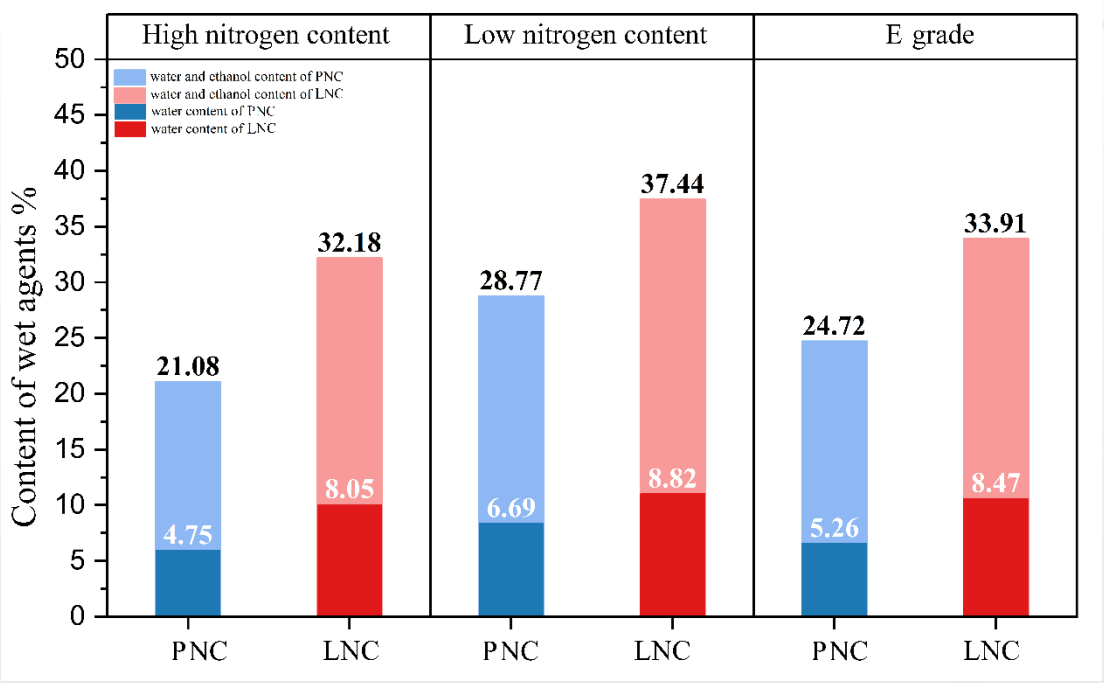
comparison of water content after dewatering between PNC and LNC



The picture is the PNC/LNC's water content after dewatering in same condition

1. The water content after dewatering of the PNC samples was about 7-10% lower than LNC;
2. The PNC samples are more easily dewatered than the LNC samples;
3. This property of PNC is highly advantageous to industrial manufacture.

comparison of wetting agent content between PNC and LNC

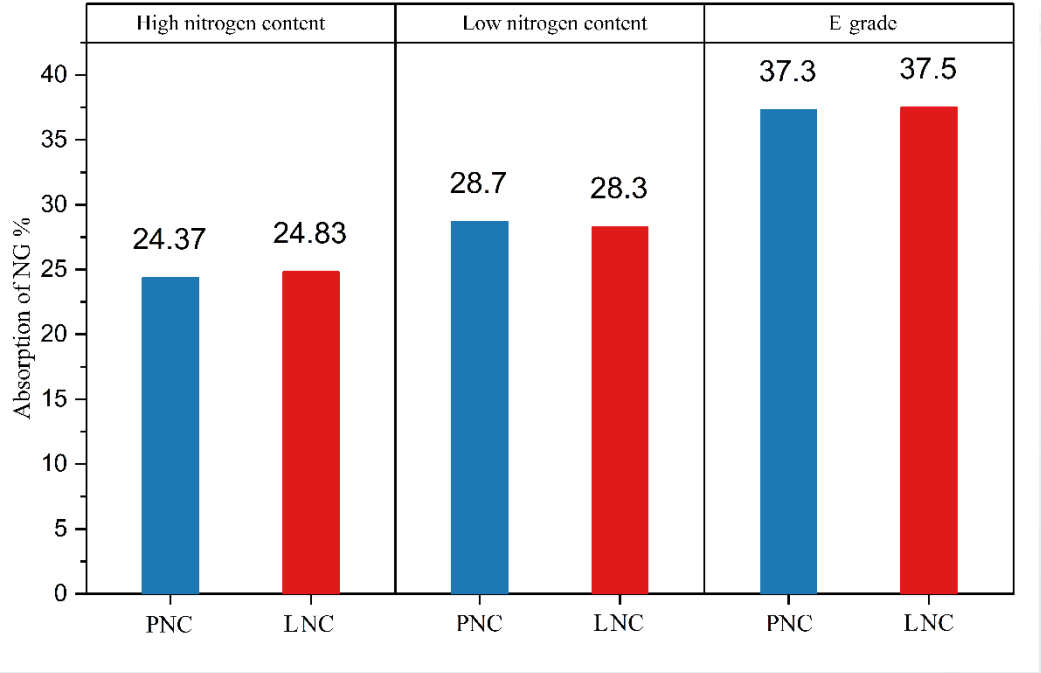


The picture is the PNC/LNC ‘s water-alcohol content after alcoholizing in same condition

1. The content of water in PNC is 2-3% lower than LNC, and the content of water and alcohol is about 9- 11% lower than LNC;
2. So PNC samples are easier to achieve dewatering and alcoholizing goal;

3 Results and Discussion

Comparison of NG content after absorption between PNC and LNC



PNC's Absorption of NG

1. There is no significant difference in the ability to absorb nitroglycerin (NG) between the PNC sample and the LNC sample in same condition;
2. The ability of PNC to absorb NG meets the requirements for current propellants' producing.

4 Conclusion

1. Standard

- All parameters of PNC samples reach excellent level and meet the requirements of ČOS 137605 and MIL-DTL-244C. standards.**So it is feasible to eliminate the deflaking process to prepare NC by using pulverized cellulose.**

2. Reactivity

- The nitration of pulverized cellulose is lower nitric acid content, lower temperature , shorter time and lower acid to cellulose ratio. The nitration process is more flexible and economic.So **pulverized cellulose has excellent reactivity in nitrition.**

3. Process

- The pulverized cellulose's mobility in the slurry is good.so we can increase the content of PNC in transporting and boiling to obtain higher equipment efficiency.
- The dewatering and alcoholizing behavior of PNC is wonderful because of intact fibrous tubular structure of the PNC. **So PNC are easier to achieve dewatering and alcoholizing goal.**

5 Prospects

The process of preparing high quality PNC is feasible and even more flexible and economic.

However, a large loss of materials will happen if producing by traditional technique . Therefore, three following technologies need to be developed and validated.

1. The technology of deaciding in PNC manufacture.

2. The **technology of** preventing product loss during the washing, concentrating and dewatering processes.

3. Application experiments of PNC in gun propellants and rock propellants producing.

Thank you