Journal of Hazardous Materials, 13 (1986) 17—26
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ASSESSMENT OF THE EXPLOSION HAZARD DURING CONTINUOUS PURIFICATION OF NITROCELLULOSE IN THE CONICELL*

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(Received January 16, 1985; accepted May 26, 1985)

Summary

As part of the overall Army Modernization program, a Conicell production unit was evaluated for continuous purification of military grade (12.6 N or 13.4 N) nitrocellulose (NC) at Radford Army Ammunition Plant (Radford AAP). In the Conicell, trace residual acid is removed from NC fibers by circulating a 1:9 ratio of NC in hot (130°C to 140°C) water under approximately 45 psig to 100 psig pressure. Soda ash is also added to neutralize acidity. The Conicell process is expected to reduce NC purification costs by reducing cycle times, energy requirements, water usage and improve process control. System safety analyses of the Conicell equipment design and control system [1] identified potential hazards which could result in equipment damage or personnel injury. Simulated tests were conducted to assess no-flow (settled NC layer in pipe) and plug conditions. Tests simulating a plugged condition determined that unboiled and uncut NC in contact with 190°C steam jacketed pipe surfaces would decompose rapidly enough to overpressurize and damage equipment. Loop flow monitors, an improved emergency flush system, control room protective shield and other minor equipment changes to permit remote operation were incorporated into the Conicell design to achieve acceptable risks for MPBMA OSM 385-1 [2] Hazard Categories I, II and III accidents.

Introduction

Conventional manufacture of NC includes two purification operations known as viscosity (acid) boiling and poaching (Fig. 1). These operations extract trace residual acid from the NC fibers to improve its long-term stability and decrease its viscosity for processing. The extraction process is slow and requires long cycle times at atmospheric pressure. Processing large quantities of NC therefore requires a number of large boiling tubs, and considerable amounts of water and energy to heat water, stir the NC, etc. Tests by various researchers [3] demonstrated that NC purification can be achieved much faster by using higher pressures and temperatures than those used in the batch process. A European designed Moser continuous NC purification unit (Conicell) was installed and modified for evaluation

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*Paper presented at the 1985 ADPA Joint Symposium on Compatibility/Processing of Explosives and Ingredients, March 11—13, 1985, Hilton Head, SC, U.S.A.

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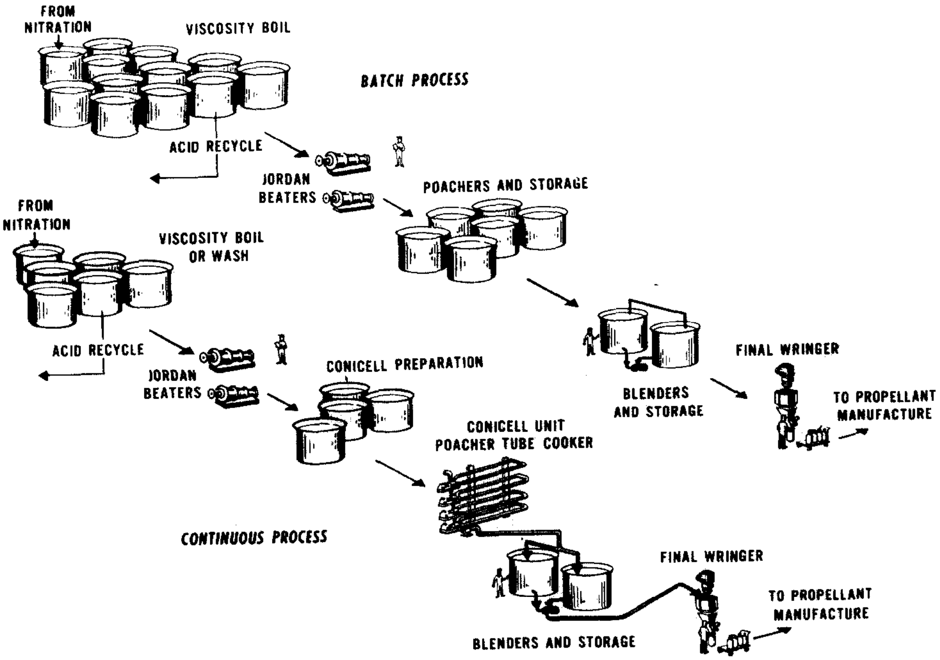

Fig. 1. Nitrocellulose manufacturing - purification flows.

at Radford AAP. This unit is designed to process 2000 pounds of NC per hour at higher temperatures and pressures.

Present studies [4] indicate that low grade (12.6 N) and high grade (13.4 N) NC can be acid boiled for one-half the conventional cycle time, cut in the Jordan mill and then poached in the Conicell. In the Conicell process, the potential exists for the formation of a settled layer or plug of NC which contacts steam heated piping. This paper discusses the results of testing conducted to determine the reactivity and system damage for NC layer or plug situations due to NC decomposition in the presence of a copious quantity of water.

Potential hazard

A total system safety analysis of the Conicell operation identified the potential for thermal NC decomposition if an NC layer or plug developed within steam (190°C) jacketed recirculation loops. Table 1 shows that exposure of dry NC to temperatures above 125°C will result in some NC decomposition [5]. Exposure of dry NC to temperatures in excess of 170°C will result in explosive decomposition [6]. The decomposition rate and reaction severity of greater than 80 percent water-wet NC containing trace amounts of nitrating acid and in the confines of the Conicell was not known. If decomposition occurs at a slow, or moderate rate, then decomposition gases would vent from the Conicell and no equipment damage or personnel injury should occur. The event would be designated an inconsequential Category IV accident and no additional safety modifications would be required to protect equipment or personnel. However, if explosive decomposition occurs then the potential for equipment damage and personnel injury is likely, the event would be designated as a Category IIIα/IIβ accident and safety modifications would be required. Tests were conducted to simulate NC layer and plug conditions in the Conicell and to define the reaction severity.

TABLE 1

Thermal decomposition of NC. The effect of heating on dry NC (1 g) decomposition [5]

Heating temperature, °C	Heating time, h	Gas evolved cm^3/g	Weight loss, %	Nitrogen loss, %
125	150	162	49.7	64
135	150	236	61.8	83
140	40	310	66.5	91
150	20	325	70.2	98

NC decomposes after exposure to a temperature of 170°C for 5 s [6].

Test description

NC layers and NC plugs were subjected to simulated confinement, temperatures and pressures expected during NC purification in the Conicell. These tests were conducted in the 24-inch long, 4-inch stainless steel pipe shown in Fig. 2. Electrical resistance wire insulated with ceramic beads was used to heat the test fixture to ~190°C. Pipe wall temperatures were

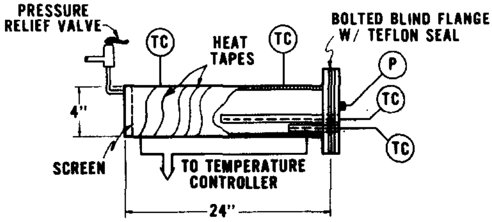

Fig. 2. Test fixture. (Note: The test fixture is schedule 40, STT pipe with a welded plate at vented end.)
Legend: TC - thermocouple: P - pressure transducer.
Test comments: (1) No mixing during test. NC layered in vicinity of screen for ~4% NC in water tests. (2) The NC plug was ~20 inches long with water filling void spaces. The plug water content ranged from 77 to 86 percent. [Note: Test 6 — only a 6-inch long cake (plug) of NC was tested.] (3) After testing any remaining NC was sent to lab for a TV analysis. (4) The test fixture shell was heated to 185—190°C (150 psig saturated steam temperature).

monitored by thermocouples. Long and short thermowells were used to monitor internal temperature at two locations. Internal pressure was controlled by a spring loaded pressure relief valve preset to open at pressures ranging from 45 psig at the pressure control valve (top of the unit) to 100 psig in the first recirculation loop (bottom of the unit).

NC was loaded into the fixture as discussed in the following:

NC Layer — NC:water slurries containing up to 10 percent NC were poured to completely fill the fixture. NC was permitted to settle out to form a layer in the fixture. Typically, the NC layer still contained ~88 percent water and occupied ~95 percent of the pipe cross-sectional area.

NC Plug — Water-wet NC was manually squeezed to wring excess water from it and tamped into the test fixture. Before closing the fixture, water was added to fill space between the NC plug and flange.

NC in the test fixture was heated to and held at the desired temperature and pressure for two hours unless an explosive reaction occurred before the end of the test period.

Tests were conducted using nitropulp and nitrocotton available from conventional NC manufacturing facilities at Radford AAP during the test period. Most tests were conducted using high grade (13. 4 N) NC which is considered to be most likely to react explosively and result in conservative test results. Unstabilized (not acid boiled) NC and partially stabilized (acid boiled but not poached) NC were tested. Although all NC will be cut into shorter fiber lengths (Jordan Mill) before processing in the Conicell, there was no approved method of cutting unstabilized NC during the initial test period. Therefore, most unstabilized NC tests were conducted using uncut and water-washed NC from the nitration operation. In order to minimize test costs, no attempt was made to test all possible combinations of variables. Only worst case scenarios were evaluated to establish if an explosive reaction is likely to occur.

Discussion

NC layer decomposition

No explosive reaction occurred during eight tests conducted with unpurified and partially purified NC (13.4 N and 12.6 N) settled from slurries containing up to 10 percent NC (see Table 2). The viscosity of recovered NC was reduced to $\leqslant 0.1$ s as measured by the falling ball method. The moisture content of recovered NC after tests with the 45 psig relief vent ranged from 35 to 72 percent.

Complete degradation of NC occurred during tests with the 100 psig relief vent and only black colored water was recovered after the tests. It is hypothesized that an explosive reaction did not occur during these tests because free water moderated the initial NC decomposition at the fixture

TABLE 2

NC thermal decomposition tests at elevated temperature and pressure

Test No.	NC type	Nitration level, %	Acid boiled	Cut in Jordan beater	%NC in slurry	Test configuration	Relief pressure, psig	Reaction	Fixture damage
1	Nitropulp	13.4	yes	yes	4	settled layer	45	orderly decomposition	no
2	Nitropulp	13.4	yes	yes	4	settled layer	100	orderly decomposition	no
3	Nitropulp	13.4	no	yes	10	settled layer	45	orderly decomposition	no
4	Nitropulp	13.4	yes	yes	23	plug	45	orderly decomposition	no
5	Nitropulp	13.4	yes	yes	18	plug	100	orderly decomposition	no
6	Nitropulp	13.4	no	no	15	plug	35	explosion	yes
7	Nitrocotton	12.6	no	yes	10	settled layer	45	orderly decomposition	no
8	Nitrocotton	13.4	no	no	3.6	settled layer	45	orderly decomposition	no
9	Nitrocotton	13.4	no	no	4	settled layer	100	orderly decomposition	no[a]
10	Nitrocotton	13.4	no	no	4	settled layer	100	orderly decomposition	no
11	Nitrocotton	13.4	no	no	4	settled layer	45	orderly decomposition	no
12	Nitrocotton	13.4	no	no	18	plug	45	explosion	yes

[a] Some pressure loss due to leaking through thermowell threads.

wall to a rate slow enough to prevent pressure buildup in the fixture. By the time free water boiled away (if all of it boiled away) partly decomposed NC and/or char built up at the NC—wall interface to thermally insulate unreacted NC from explosive temperatures. Continued heating apparently resulted in progressive drying and decomposition of NC in the interior of the fixture, but at a temperature and rate slow enough to preclude an explosive reaction (i.e. evolution of decomposition gases at a rate slow enough to vent from the fixture via the pressure relief valve without significant pressure buildup within the fixture). Test number 7 in Table 2 is shown in Fig. 3 showing how fixture and thermowell temperatures behaved during these tests.

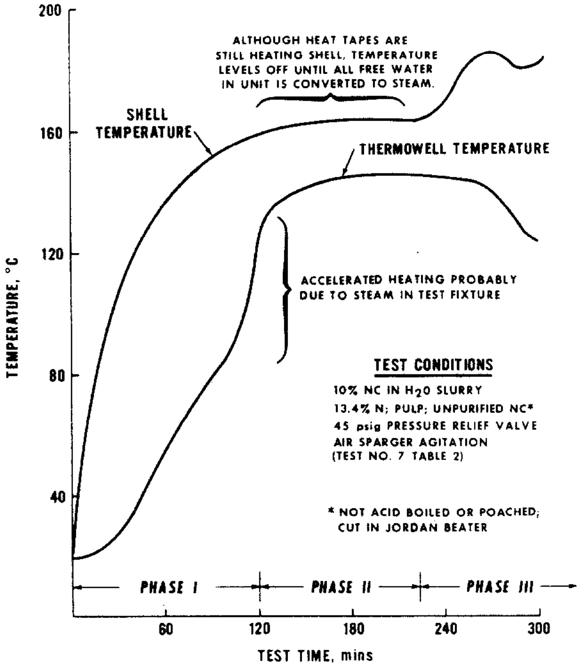

Fig. 3. Typical Conicell test phases.

Testing usually proceeded in three phases.

Phase I — The heating phase (Phase I) lasted one to two hours. During this phase, both the fixture and thermowell temperatures increased; the thermowell temperature lagged well behind that of the fixture. This portion of the test is not representative of Conicell operating conditions because NC slurry in Conicell loops is maintained at 140°C.

Phase II — During the steaming phase (Phase II) the fixture and thermowell temperatures levels off. It is hypothesized that the temperatures are controlled by conversion of free water in the fixture to steam. The relief valve limits steam pressure inside the fixture. Therefore, the interior temperature of the fixture should be that of saturated steam at the set-point pressure of the valve. Note: The temperature of saturated steam at 35 psig is 125°C; at 45 psig is 140°C; at 100 psig is 160°C.

Phase III — During the high temperature phase (Phase III) fixture temperatures increased and had to be controlled to ~190°C by the temperature controller. During this phase, the thermowell temperature began a moderately slow decline. It is thought that all water was boiled out of the NC in contact with the hot fixture wall, and dry NC on the fixture wall acted as a thermal insulator between the fixture wall and NC surrounded by the insulating layer. As the insulating layer thickened, the interior temperature continued to decline. The presence of a thermal gradient through the NC layer was verified by visual inspection of NC remaining in the test fixture after some of the tests. Discoloration of NC due to decomposition ranged from black, charry residue on the fixture wall, to increasingly lighter shades of brown, and finally to white (relatively undecomposed) NC at the center of the NC mass.

On the basis of the above, it was concluded that unpurified or partially purified, cut or uncut, nitropulp or nitrocotton layers within heated Conicell loops will not thermally decompose fast enough to react explosively.

NC plug

Two of four tests simulating an NC plug in a Conicell loop resulted in an explosive reaction and some test fixture damage. Both explosive reactions involved tests with unpurified and uncut NC (13.4 N) plugs containing (initially) 82—85 percent water. Examination of damaged fixture components and the absence of component fragmentation indicates that only a rapid overpressurization of the fixture occurred and that there was no detonation reaction. Recovery of some water-wet and still white NC after the explosive reactions indicates that a non-propagating and localized decomposition reaction occurred in the fixture; probably at the NC—pipe wall interface. The high pressure reactions occurred twenty to forty minutes after the NC temperature leveled off (Phase II heating). Figure 4 shows the fixture shell and thermowell (NC) temperatures during test 12 (Table 2) which resulted in fixture damage.

Simulated NC plug tests 4 and 5 (Table 2) did not react explosively. These tests were conducted using partially purified, cut nitropulp (13.4 N) more like that processed in the Conicell.

It is evident that the unstablized NC is more reactive than acid boiled

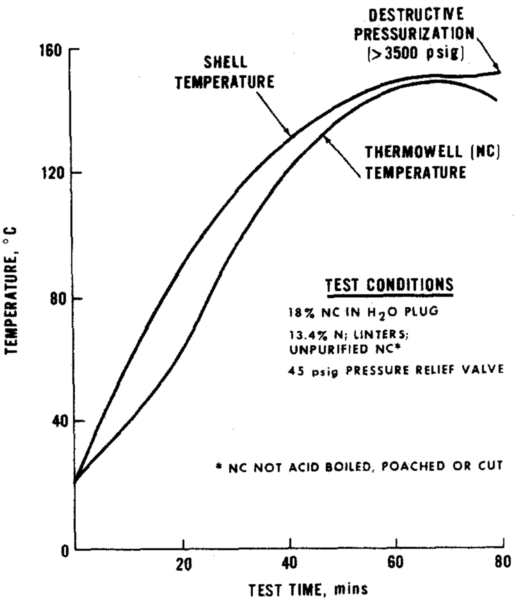

Fig. 4. Conicell test No. 12.

NC and is more likely to cause an explosive reaction in the Conicell. However, the limited number of tests conducted with acid boiled NC is insufficient to rule out the possibility of an explosive reaction for all plug conditions. It is concluded that there is a risk of an explosive reaction in the Conicell if plugging occurs and the plug condition is not quickly detected and flushed from the loop.

Application

To minimize the risk of an explosive reaction during Conicell operations and provide additional protection to personnel, the following equipment changes were incorporated into the Conicell design:

1. An ultrasonic flow detector was installed on each loop to monitor flow directly and detect loss of flow for a plugged condition or pump failure. The detectors are interlocked to turn the emergency flush system ON if a no-flow condition is detected. The flow detectors may also indicate the presence of an NC layer in a loop since reduced cross-sectional area will increase resistance to flow and change the flow velocity.
2. The loop emergency flush system was upgraded to provide positive and faster loop flushing with cool water. The new system can exert up to 1.25 tons of hydraulic force on one side of a plug (calculated pressure drop of ~88 psig across the plug) which should be sufficient to breakup or force the plug from the loop. With the new design, an unbroken plug can exit the loop via the larger emergency flush discharge

system. The modified emergency flush system was tested and found to function very well. The modified flush system will cool Conicell loops to <100°C within approximately one minute, flush most of the NC from the system in 2 to 3 minutes and is a great improvement over the original flush system.

3. A common wall between manned (control room and decant bay) and unmanned (Conicell bay) operations was reinforced with 1/4-inch thick steel plate and 1-1/4-inch thick Lexgard bullet-proof laminate windows to protect operators from missiles if an explosive reaction occurs.
4. Procedures have been revised to prohibit personnel from entering the Conicell bay during operations. A differential pressure switch was also installed in the emergency drown system stand pipe to permit remote monitoring of water level in the control room.

Conclusion

These tests determined that water-wet, unpurified NC jammed against 190°C steam jacketed piping (plug condition) may react explosively and cause equipment damage. Equipment and procedural changes were instigated to minimize the risk of equipment damage or personnel injury during Conicell operation. These changes have reduced the probability of a IIIα/IIβ incident from an unacceptably high $1.0/1 \times 10^{-2}$ per hour of operation to an acceptable low $1 \times 10^{-4}/1 \times 10^{-7}$ per hour of operation which now meets the maximum allowable accident risk requirements of MPBMA OSM 385-1.

Glossary

Conicell	—	Continuous NC purification equipment designed by Moser Processing, Corseaux, Switzerland
Military grade NC	—	NC nitrated to levels including 12.6% and 13.4% nitrogen
Hazard Categories	—	Degrees of accident consequence. Category I (catastrophic) is worst case, etc.
Jordan mill	—	Machine for cutting NC fibers into shorter lengths
Nitrocellulose (NC)	—	Generic name for any form of nitrated cellulose
Nitrocotton	—	NC made from cotton linters cellulose
Nitropulp	—	NC made from wood pulp cellulose
NC residual acid	—	Small amounts of nitric and sulfuric acid retained within hollow NC fibers
Purification (NC)	—	Removal of all traces of acid from NC fibers
Soda ash	—	Sodium Carbonate (Na_2CO_3)

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