

Andrew Sanderson



Start-up of a New Efficient and Green TNT Manufacturing Process

Andrew J. Sanderson¹, Dick Rentfrow¹, Peter Wesson¹, Gene Johnston², Timothy Frazier¹ and Greg Startzell¹

¹ATK Ammunition and Energetics
Radford, Virginia

²ATK Thiokol Promontory Operations
Brigham City, Utah

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The result of the ATK TNT project has been the construction and start-up of a new flexible explosives manufacturing capability within two years of contract award.

- This facility has extensive safety controls and unequaled environmental compliance in the manufacturing of TNT.

During its very first run the new process made higher purity TNT than has ever been seen before from any previous US production facility.

- Previous operation start-up took a year to make spec TNT

On its third test run, over 10,000lb of Mil Spec TNT was manufactured and packaged. This TNT was 100.00% pure by gas chromatographic analysis.

| | New Process | Old Process |
|---------------|------------------------------|------------------------------|
| TNT Purity | 100.0%(nominal) | 99.8%(Max) |
| Air Emissions | NOx 0.2lb/hr CO <2.5lb/hr | NOx 166lb/hr CO 110 lb/hr |
| Red Water | None | 8500 gal/day |
| Non-spec. TNT | 0 | Up to 10% |

Objective:

Design and build a TNT manufacturing plant per proposal to US DoD

- **Safe, Green Process**
- **Flexible Design for manufacture of other energetics**

Requirements

The US DoD required a flexible energetics facility capable of making up to 15Mlb/yr of Mil Spec TNT.

The user requires TNT to fill ordnance in existing equipment and obtain high quality fills. This requires consistent purity (set point) and flake size (thickness and max dimension) product.

Environmental requirements constrained the emissions of waste and by-products (red water, CO, VOC, NO_x and SO_x, waste water (acidity and organic content), and steam usage.

Obtain VOC - Use IPT and 6 sigma tools throughout design, construction, start-up

Trade Studies

- Search for best practices
- Obtain data on potential improvements
- Use data based decision analysis tools to select optimum solutions

Use formal PDR, CDR, PRR processes

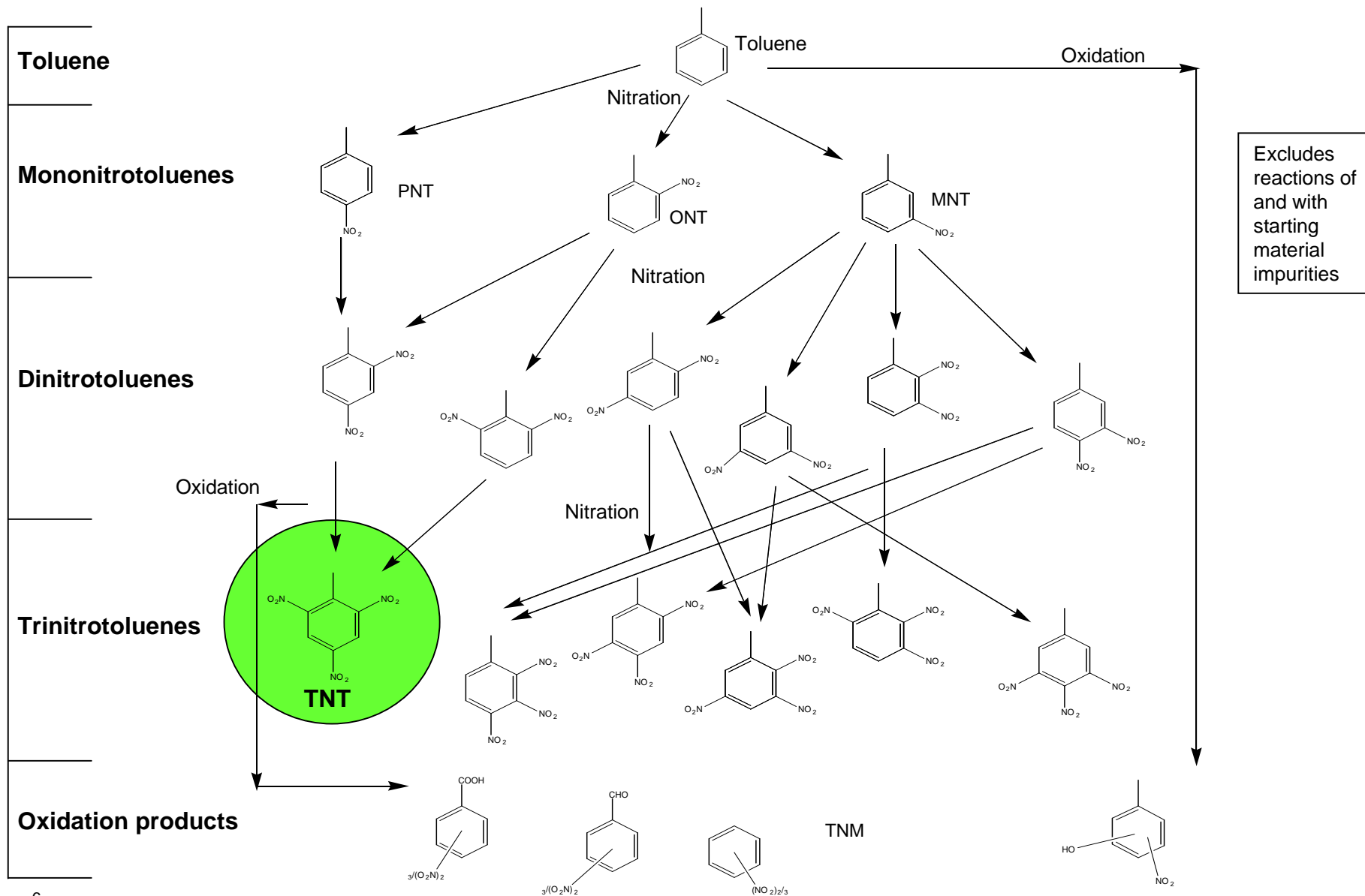
Detailed Hazards Analysis

Select and train technical operators to drive quality in production

TNT Chemistry



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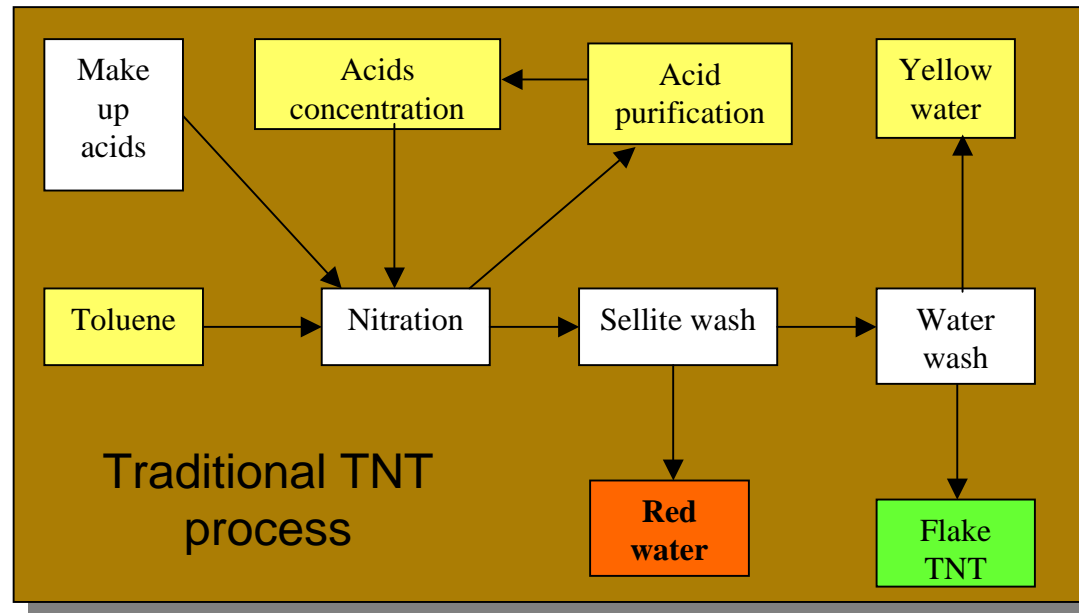
Traditional TNT manufacturing is extremely “dirty”

Waste from traditional TNT production has severe environmental consequences

- K047 prohibited from land disposal 40 CHR Ch. 1 §286.33
- Yellow water
- Air emissions, TNM, CO, NO_x, VOC

Alternatives have been used historically that could be employed to avoid some issues

- Purification by crystallization
- Yellow water minimization
- Alternative starting material
- Batch nitration

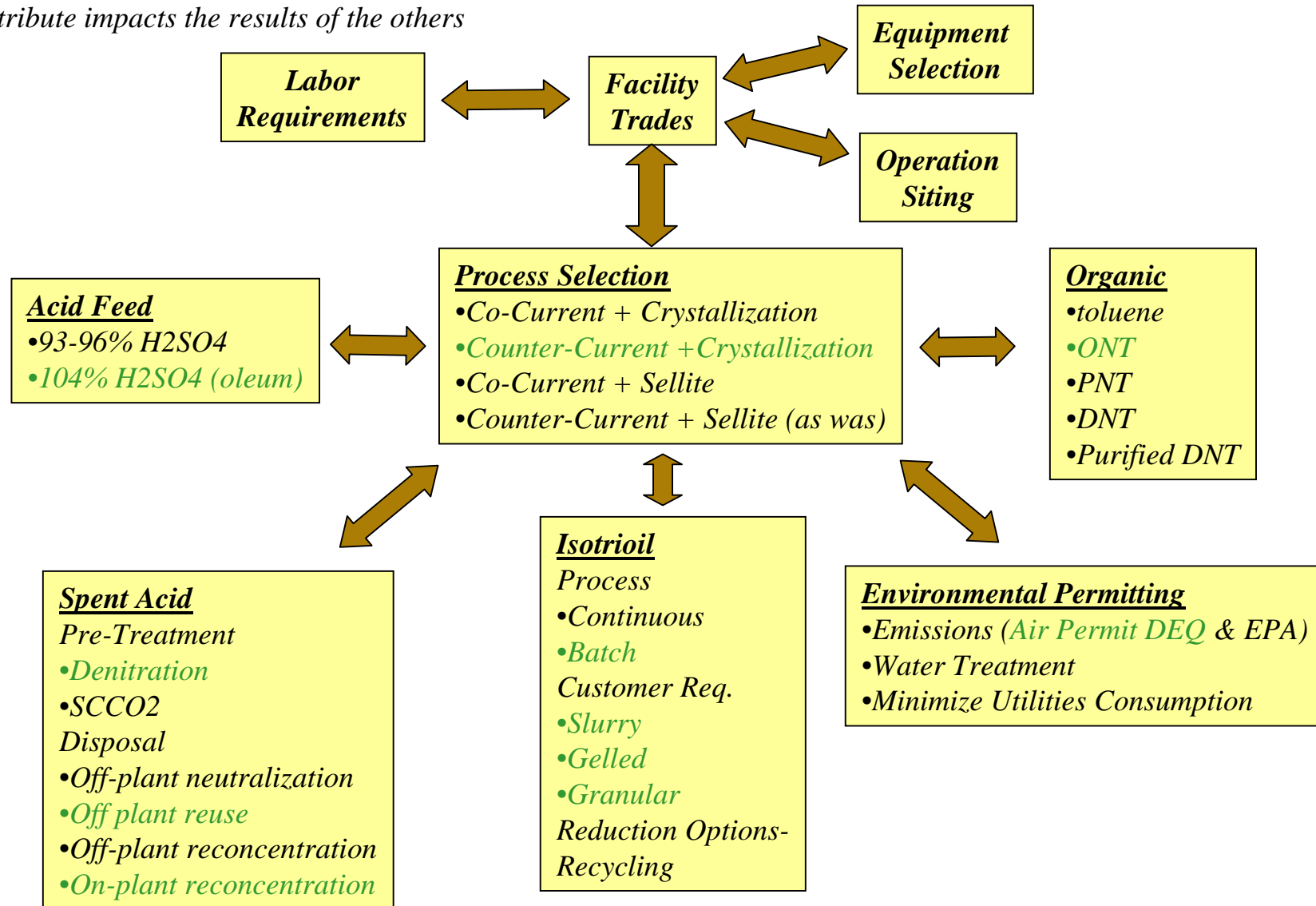


TNT Trades Relationships



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Each attribute impacts the results of the others



Tabulate options with detailed analysis, including

- Safety
- Environmental
- Capital and recurring costs
- Impact on other processes
- Technical, schedule, and cost risks
- Human factors
- Use Pugh tables and weighted Pugh tables as appropriate
- Communicate with IPT and customer

| Option | Denitration | CO2 extraction | Spent to .. | Notes |
|--------|-------------|----------------|-----------------------------------|--|
| 1 | Yes | Yes | RFAAP NAC/SAC then for sale | Limited NAC/SAC capacity |
| 2 | Yes | No | Dupont | |
| 3 | Limited | No | AP | With DNT use |
| 4 | Yes | No | GEA | |
| 5 | Yes | No | GEM | |
| 6 | Yes | No | RFAAP NAC/SAC then for sale | Needs low organics level from Deni |

Starting materials received by rail (truck is also possible) with significant storage possible

Nitration and purification

- Counter current, ONT, anhydrous mixed acid, nitric acid crystallization
- No red or yellow water

Product finishing, as previous drum flaking with new automated boxing

Isotriol (TNT impurities) to separate flexible batch treatment and pack out facility

Vapor and spent acid to new denitration and air treatment facilities

Scrubber and similar water to dedicated waste water treatment then plant biological waste water treatment

Process monitoring, quality control and process improvement from control room at area laboratory with chemists running new laboratory, PLC and main operations

Siemens PCS7 System implemented for TNT manufacturing control

Fiber Optic network connects all manufacturing and support nodes

Nitration and Purification, Spent Acid Denitration & Fume Abatement monitoring and control from two locations

Modernized, automated TNT finishing and pack out controlled locally, with data linked to PCS7 system

Complete data acquisition included (historical trending, SPC charting and integration with LIMS for lab data)

Expansion capability for future energetics manufacture



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ACCOMPLISHMENTS

CDR complete in 9 months from contract award

Facility constructed and operational 2 years from contract award

- 1000 process I/O, >150 interlocks
- Chemical sampling on every vessel and line
- Unique solutions to air emissions

Provided lab data for Hazards Analysis

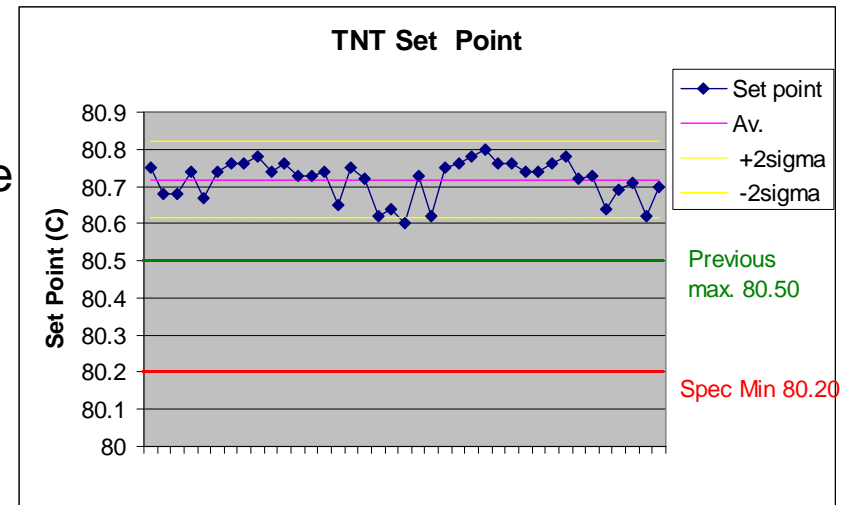
Built and equipped a laboratory

- Recruited and trained staff; developed, documented, and validated methods

Currently in Preproduction Initial Production

Integration of operations and technical staff to drive operation efficiency and quality

Still discovering improvements



Operations per Building



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A mixture of original buildings with new equipment and entirely new buildings/operations



ONT in



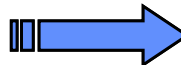
Isotriol 9505



N&P 9501



Finishing 9504



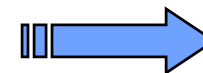
Pack out



Acids in



Denitration



CO/TNM destruct

Area Office



Laboratory/control room 9562

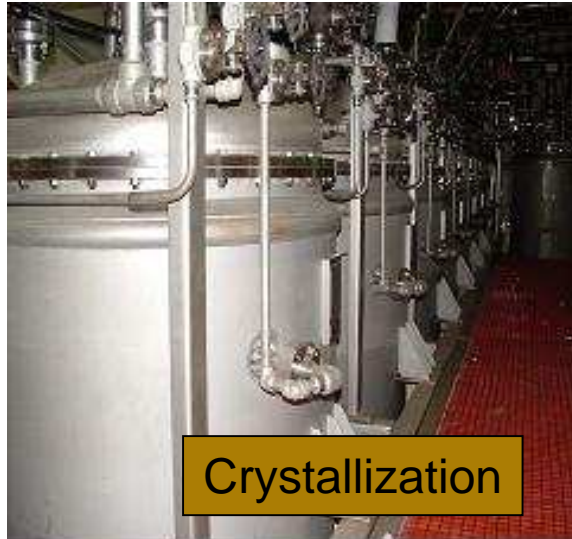


Maintenance

Nitration and Purification



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Crystallization



Filtration



Washing



Nitration

Sample points at every vessel (unless under vacuum) and line

Each sample point has nominal values for composition with max and min

Each sample point has a sampling procedure and test procedure for the sample

Troubleshooting guide for out of nominal process conditions

PLC Control and Alarm System



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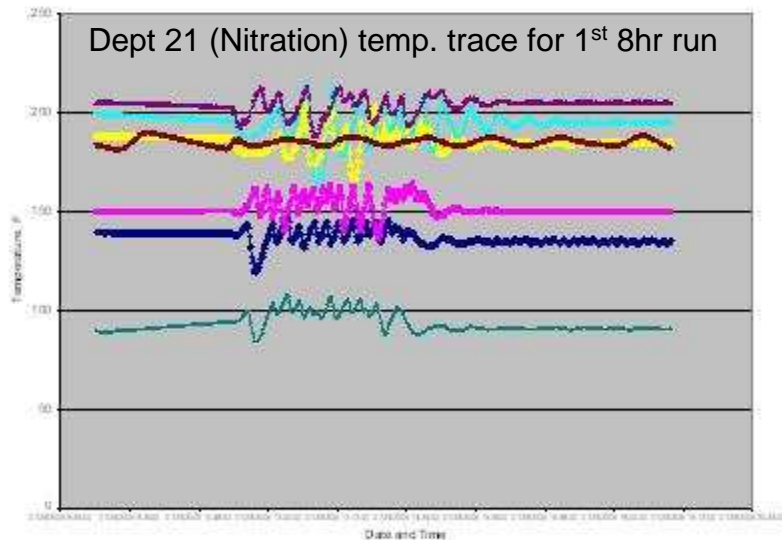
The PLC controls N&P by monitoring raw material flow, speeds, pressures, and temperatures

Upset conditions instigate an alarm on PLC in corresponding department (process)

Emergency conditions sound an alarm and an alert on PLC screen

Multiple levels of alarms:

- Vent system interlocks:
 - high—stop raw material feed
 - high high—increase cooling water supply to jacket of vessel
 - high high high—immediate dump/drown



The New facility has >50x reduction in emissions to air

The crystallization completely eliminates red water emissions with a much more robust purification process

Yellow water is eliminated by reuse in the nitration process before integration in the spent acid (reducing organics in the spent acid at the same time)

| Emissions (TPY) | Old Facility | New Facility | Delta (% reduction) |
|-----------------|--------------|--------------|---------------------|
| NOx | 633.6 | 0.75 | 632.8 (99.9%) |
| CO | 416.7 | 10.95 | 405.8 (97%) |
| TNM | 40.6 | 0.83 | 39.7(98%) |

TNT LAT and Process Testing



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Type I TNT Specifications (MIL-DTL-248D)

Lot Acceptance Testing according to MIL STD 650

Form – Flake

- Visual, subjective

Color - No darker than FED-STD-595 Color Standard No. 30257

- Visual, subjective

Solidification Point, °C - 80.2 min

- Manual measurement

Moisture, % - 0.10 max

- Automated Karl Fischer titration

Acidity, % as H₂SO₄ - 0.02 max

- Manual titration with caustic to a bromothymol blue endpoint after organic dissolution and aqueous extraction

Alkalinity - None

Insoluble Matter, % - 0.05 max

- Gravimetric with organic dissolution and filtering

Sodium, % - 0.001 max

- Atomic absorption spectroscopy (FAA)

Flake Thickness, inch - 0.04 max with an average of 0.025 max

- Manual measurement with micrometer

Flake Size - 100% passing through 3/8" mesh sieve

In-Process Testing in the Laboratory

30 Routine Samples per Day

| | Sample Point | Test |
|---------------------|--------------------------------|----------------------------------|
| 1/nitrator/shift | 2101A-5A | Acid, H ₂ O, Organics |
| AcidWashOF to Cryst | 2107A | Organics |
| AcidWash | 2107B | Acid, H ₂ O, Organics |
| Extractor | 2113A | Acid, Organics |
| ONT/DNT Tk | 2117 | HPLC |
| AcidMake-Up Tk | 2130 | Acid |
| WaterWashedTNT | 2316 | HPLC |
| Acid Tanks | T2318-20 | Acid |
| WNA | 2322, 2324 | Acid, Organics |
| YellowWater | 2401B-03B | Acid, Organics |
| Isotrioil | Product | HPLC |
| Isotrioil | WasteWater | HPLC |
| Denitration | H ₂ SO ₄ | Acid, Organics |
| Denitration | HNO ₃ | Acid, Organics |
| Denitration | Condenser | Acid, Organics |
| Denitration | Reflux | Acid, Organics |
| Fume Abatement | | Acid, Organics |

In-Process Testing in the Production Area

42 Routine Samples per Day

| | Sample Point | Test |
|------------------|--------------|------------------------------------|
| 1/nitrator/shift | 2101A-5A | Visual(Acid/Org) |
| 1/nitrator/shift | 2101B-5B | Visual(Acid/Org) |
| 1/nitrator/shift | R2101-5 | Visual(Acid/Org Ratio) |
| AcidWashOF | 2107A | Visual(Acid/Org) |
| AcidWash | 2107B | Visual(Acid/Org) |
| AcidWash | T2107 | Visual(Acid/Org Ratio) |
| Extractor | R2113 | Visual(Acid/Org Ratio) |
| Extractor | 2113A | Visual(Acid/Org) |
| Extractor | 2113B | Visual(Acid/Org) |
| PreCrystalizer | T2201.02 | Visual for Granules |
| TNT Washers(YW) | 2401A-03A | Visual for YW/Organic |
| TNT Washers(YW) | 2401B-03B | Visual for YW/Organic |
| TNT Washers(YW) | T2401-03 | Visual YW/OrganicRatio) |
| Emulsion Tank | T2410 | Visual (H ₂ O/OrgRatio) |

Six samples tested per day + One 5-Sample Composite
Sample Schedule determined by Mil Spec

Process control/monitoring samples points, sample schedule,
testing time, and operating limits identified and methods
developed

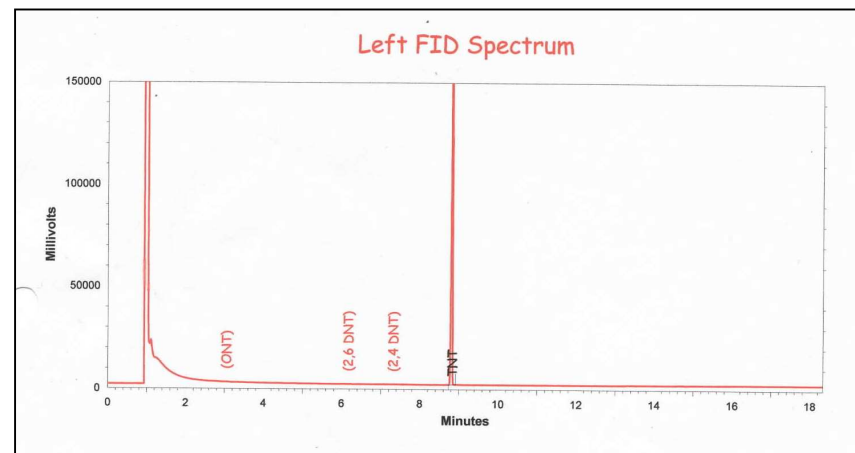
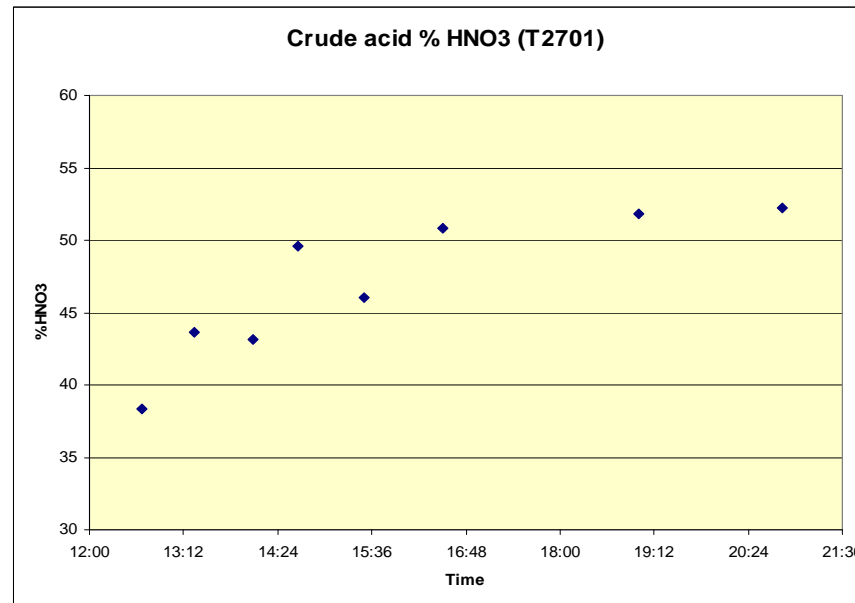
Chemical Data from First 8hr Run



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Routine, detailed near real time TNT chemical process data has never been part of production before
 TNT of this purity has never been available in the US
 The product being pure does not mean the process is perfect

| Vessel/line | Time | NB | TNT | 24DNT | 26DNT | ONT | TNM | Others | SA | NA | NS |
|---------------------------|--------|---------------|--------|--------|--------|-------|-------|---------------|--------|-------|-------|
| R2101 | 9:40 | 1.16 | | | | | | | 67.57 | 6.31 | 3.8 |
| R2101 | 12:20 | | 7.33 | 23.23 | 9.86 | 59.58 | 0 | | | | |
| R2101 | 23:59 | | 4.128 | 23.616 | 7.326 | 64.93 | | | 65.59 | 7.456 | 2.53 |
| R2102 | 20:35 | 6.78 | | | | | | | 81.55 | 5.42 | 2.66 |
| R2102 | 12:20 | 5.87 | | | | | | | 78.45 | 9.38 | 4.01 |
| R2102 | 12:20 | | 29.02 | 42.92 | 28.07 | 0 | 0 | | | | |
| R2102 | 23:59 | | 16.096 | 60.3 | 23.604 | 0 | | | 81.876 | 3.861 | 3.401 |
| R2103 | 18:35 | 8.54 | | | | | | | 85.75 | 8.86 | 2.65 |
| R2103 | 12:20 | 11.7 | | | | | | | 84.31 | 8.39 | 2.5 |
| R2103 | 23:59 | | 62.761 | 29.57 | 7.668 | 0 | | | 86.198 | 1.019 | 2.833 |
| R2103 | 15:10 | 4.38 | | | | | | | 72.51 | 9.09 | 1.52 |
| R2104 | 20:35 | 5.96 | | | | | | | 89.98 | 7.26 | 1.63 |
| R2104 | 23:59 | | 93.395 | 5.843 | 0.762 | 0 | | | 90.904 | 4.348 | 2.354 |
| R2104 | 15:10 | 6.65 | | | | | | | 87.05 | 9.84 | 1.75 |
| R2105 | 18:45 | 12.3 | | | | | | | 92.27 | 7.42 | 0.76 |
| R2105 | 17:30 | | 98.8 | 1.2 | | | | | | | |
| R2105 | 23:59 | | 99.073 | 0.927 | 0 | 0 | | | 97.298 | 7.463 | 1.225 |
| R2105 | 15:10 | 8.93 | | | | | | | 87.64 | 9.04 | 0.9 |
| SV 2115 (extractor SA)? | 12:20 | 1.72 | 8.1 | 62.86 | 26.4 | 2.63 | 0 | | | | |
| SV 2115 (extractor SA)? | 12:45 | | | | | | | | 62.85 | 11.55 | 2.35 |
| SV2113A (extractor acid) | 12:20 | 1.67 (0.93 by | 8.04 | 63.11 | 26.6 | 2.25 | 0 | | 63.78 | 10.29 | 2.53 |
| SV2113A (extractor acid) | 14:45 | 0.105 (ext) | | | | | | | 64.55 | 8.64 | 3.18 |
| SV2113A (extractor acid) | 14:45 | 0.95 | 6.24 | 44.37 | 16.12 | 33.28 | | | | | |
| SV2113A (extractor acid) | 18:35 | 0.79 | | | | | | | 72.8 | 5.68 | 5.09 |
| T1945 | 15:15 | 0.27 | 5.3 | 29 | 63.6 | 2.1 | 0.02 | | | 82.7 | 7.81 |
| T1945 | 11:00 | | | | | | | | | 71.3 | 3.57 |
| T2001 | ? | 0.3 | | | | | | | 68.51 | 8.12 | 3.24 |
| T2001 (old method) | 25-Jan | 0.36 | | | | | | | 68.69 | 7.79 | 4.34 |
| T2001 (withLC) | 25-Jan | 1.53 | | | | | | | 69.51 | 8.11 | 4.39 |
| T2107 (acid washer) conte | 17:30 | | 99.1 | 0.9 | | | 0 | | | | |
| T2107 (acid washer) conte | 17:00 | | 98.43 | 1.31 | 0.17 | | | | | | |
| T2318 (xtallization acid) | 17:50 | | | | | | | | | 48.4 | |
| T2320 (xtallization acid) | 20:55 | | | | | | | | | 56.6 | |
| T2401 (washer 1) | 13:50 | | 100 | | | | | | | | |
| T2402 (washer 2) | 20:40 | | | | | | | | | 0.06 | |
| T2701 | 20:50 | 2.47 | 75.87 | 21.39 | 2.74 | | trace | | | 52.26 | |
| T2701 | 13:20 | 1.3 | 72.99 | 27.31 | 3.92 | 2.33 | 0 | | | 43.62 | |
| T2701 | 14:05 | 2.6 | 66.1 | 29.8 | 4.1 | | trace | | | 43.1 | |
| T2701 | 14:40 | 1.88 | 74.51 | 19.65 | 3.14 | 2.69 | 0 | | | 49.62 | |
| T2701 | 19:00 | | | | | | | | | 51.79 | |
| T2701 | 15:30 | 1.95 | 77.54 | 17.56 | 2.67 | 2.22 | 0 | | | 46.02 | |
| T2701 | 16:30 | 2.07 | 74.146 | 19.83 | 3.18 | 2.84 | 0 | | | 50.84 | |
| T2701 | 12:40 | | 79.64 | 24.54 | 2.84 | 2.01 | trace | | | 38.34 | |
| TNT flake (gc) | 9:01 | | | | | | | | | | |
| TNT flake (gc) | 18:00 | | | | | | | | | | |
| TNT flake (gc) | 17:00 | | | | | | | | | | |
| Washed Isotriol | 26-Jan | | | | | | | est pks @ 0.5 | | | |



Chemical elements to Optimize the TNT Production Process.

- Product purity – throughout process
- Yield based on ONT
- Efficiency based on all chemical reagents
- Throughput
 - Yield per unit of time and labor
- Minimize waste
 - Materials
 - By products
- Robustness
 - Doing all of the above all of the time
 - **All Models and Plans must be Based on Detailed and Accurate Process Data**

The more you understand the chemistry of the production process the safer and the more efficient you can make it become