BAE SYSTEMS

Synthesis and Process Development of NONA

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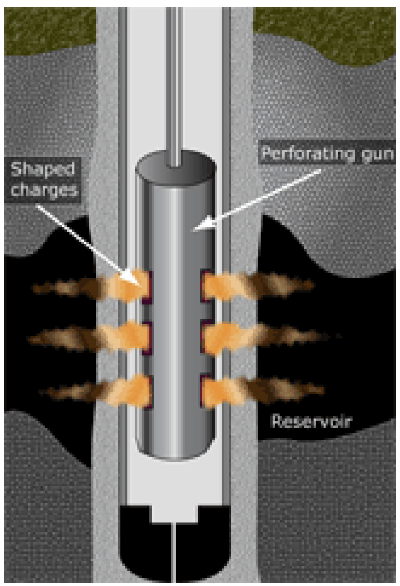
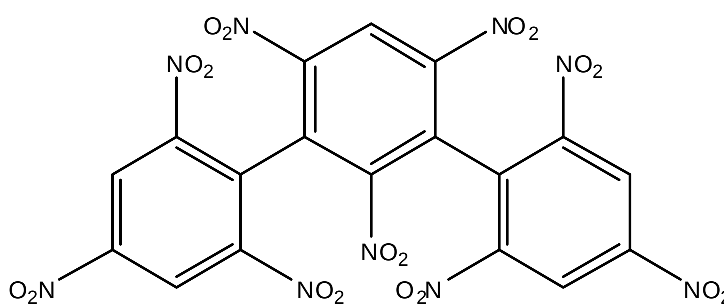
Background

- NONA (2,2',2'',4,4',4'',6,6',6''-Nonanitro-m-terphenyl) is:
  - a highly thermally stable explosive (Mp > 400°C)
  - an easily detonable explosive
- Originally developed by NOL for space applications in 1960's
  - Mostly to succeed HNS (Mp = 316°C) and DIPAM (Mp = 305°C)
- Used in Exploding Foil Initiators (EFIs), boosters, shaped charges, etc. in commercial downhole wells for oil and gas industry





Thermal Stability Evaluations

- NONA is much more thermally stable than TATB
- At temperatures higher than 200C, NONA is more thermally stable than HNS

200°C TEMPERATURE VACUUM STABILITY TESTS

Material	2	7	14	21	28	35	42	49	56	63	70	77	84	91
	Time of exposure (days). Total gas evolved (cm^3/g at STP. Average of two samples.)													
ABH[a]	.9	2.4	4.7	7.9	12.9	19.5								
BTX	.4	.9	1.5	2.0	2.4	3.1	3.9	5.0	6.2	7.7	9.9	12.0	14.6	17.6
bis-HNAB[b]	5.8	18.4												
DATB[c]	2.8	3.6	4.5	5.5	6.2	7.4	8.4	9.5	10.7	11.8	13.2	14.7	16.4	
DIPAM[d]	2.5	3.3	4.2	5.0	5.9	6.9	7.9	9.4	10.4	11.7	12.8	14.2	15.6	
DODECA	.9	1.4	1.9	2.4	2.9	3.5	4.2	6.3	7.1	7.7	8.0	8.4	9.0	9.7
DPBT[e]	.8	2.2	4.4	6.8	9.0	12.3	15.0							
DPPM	.7	1.5	2.0	2.7	4.0	5.4	6.6	7.7	9.2	9.6	10.3	10.8	11.6	12.8
HNAB[f]	.4	2.0	9.8	27.8										
HNBP	.6	1.5	2.2	3.0	3.6	4.4	4.8	6.8	7.6	8.4	9.1	9.8	10.9	11.8
HNDS[g]	2.4	15.0	,											
HNS	.4	.7	1.0	1.2	1.4	1.6	1.7	1.8	2.0	2.3	2.5	2.6	2.8	3.0
KHND[h]	.7	1.3	3.7	8.2	18.0									
NONA	.4	.8	1.1	1.6	2.0	2.3	2.8	3.2	3.6	3.9	4.3	4.7	5.1	5.4
ONT	.9	1.3	1.4	1.5	1.6	1.7	1.9	1.9	2.0	2.1	2.3	2.4	2.5	2.6
PADP-I[i]	15.0													
PATO	1.0	1.9	2.8	3.4	4.0	4.6	5.2	5.6	6.1	6.5	7.2	7.7	8.7	10.7
PENCO	.1	.2	.3	.4	.6	.6	.6	.7	.7	.9	1.0	1.1	1.2	1.4
PYX	.1	.1	.2	.2	.2	.3	.3	.4	.4	.4	.5	.6	.6	.7
TATB[j]	.3	.9	2.1	4.1	7.2	11.1	15.8							
TATB[k]	1.0	4.7	12.5	20.0										
TNN	.3	.5	.6	.8	.9	1.0	1.2	1.3	1.4	1.6	1.7	1.8	2.0	2.2
TPB	.1	.1	.2	.3	.3	.3	.3	.4	.4	.4	.5	3.2	7.0	9.5
TPM[l]	.8	4.2	7.7	11.7	15.6									
TPT	.2	.2	.4	.4	.4	.4	.5	.5	.6	.7	.9	1.0	1.0	1.1
T-TACOT	.1	.5	.9	1.3	1.6	1.9	2.1	2.5	3.0	3.5	3.9	4.3	4.8	5.3
Z-TACOT	.4	.6	.7	.8	1.0	4.1	4.9	7.1	8.6	10.8	11.2	11.4	11.5	11.5

[a] ABH terminated after 35 days.
[b] bis-HNAB aborted after 6 days.
[c] DATB terminated after 82 days.
[d] DIPAM terminated after 86 days.
[e] DPBT terminated after 42 days.
[f] HNAB terminated after 18 days.
[g] HNDS aborted after 5 days, evolved gas blew mercury into catch basin between 3 and 5 days.
[h] KHND terminated after 30 days.
[i] PADP-I aborted at 2 days, evolved gas blew mercury into catch basin in less than 2 days.
[j] TATB terminated after 42 days.

- J. F. Baytos, "High-Temperature Vacuum Thermal Stability Tests of Explosives," LA-5829-MS, Los Alamos National Laboratory, January 1975.

Performance

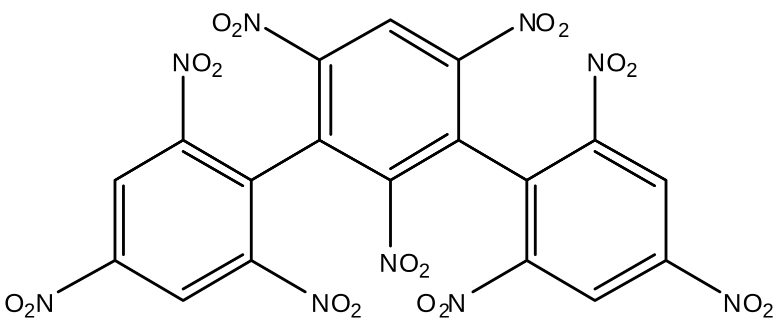
- NONA has similar explosive performance to Tetryl
- Better performance than HNS and TACOT (other thermally stable EMs)

Compound	Melting Point (C)	Density (g/cm3)	$P_{c\text{-}j}$ (kbar)	Detonation Velocity (m/s)
NONA[1]	440	1.78	255	7570 (calc)
Tetryl[2]	130	1.71	260	7850
TACOT[2]	378	1.61	181	6530
HNS[2]	316	1.60	200	6800

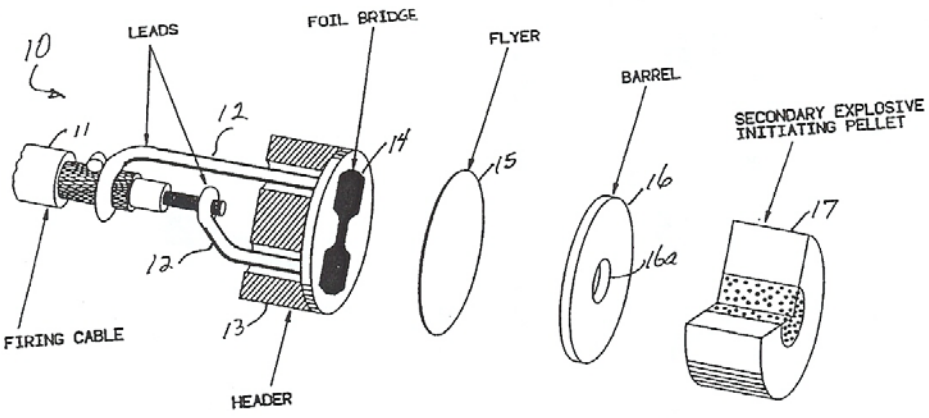
- [1] Hamid, J.; Griffiths, T.; Claridge, R.; Jordan, T. "Application of Novel Energetic Materials for Initiators and Explosive Trains", *New Trends Res. Energ. Mater. Proc. Sem*, **2004**, 133-141
- [2] Cooper, P.W.; Kurowski, S.R. "Introduction to the Technology of Explosives" Wiley-VCH, **1996**

Sensitivity

- NONA has impact sensitivity characteristics between PETN and RDX.
- NONA has impact and friction sensitivity similar to Tetryl.



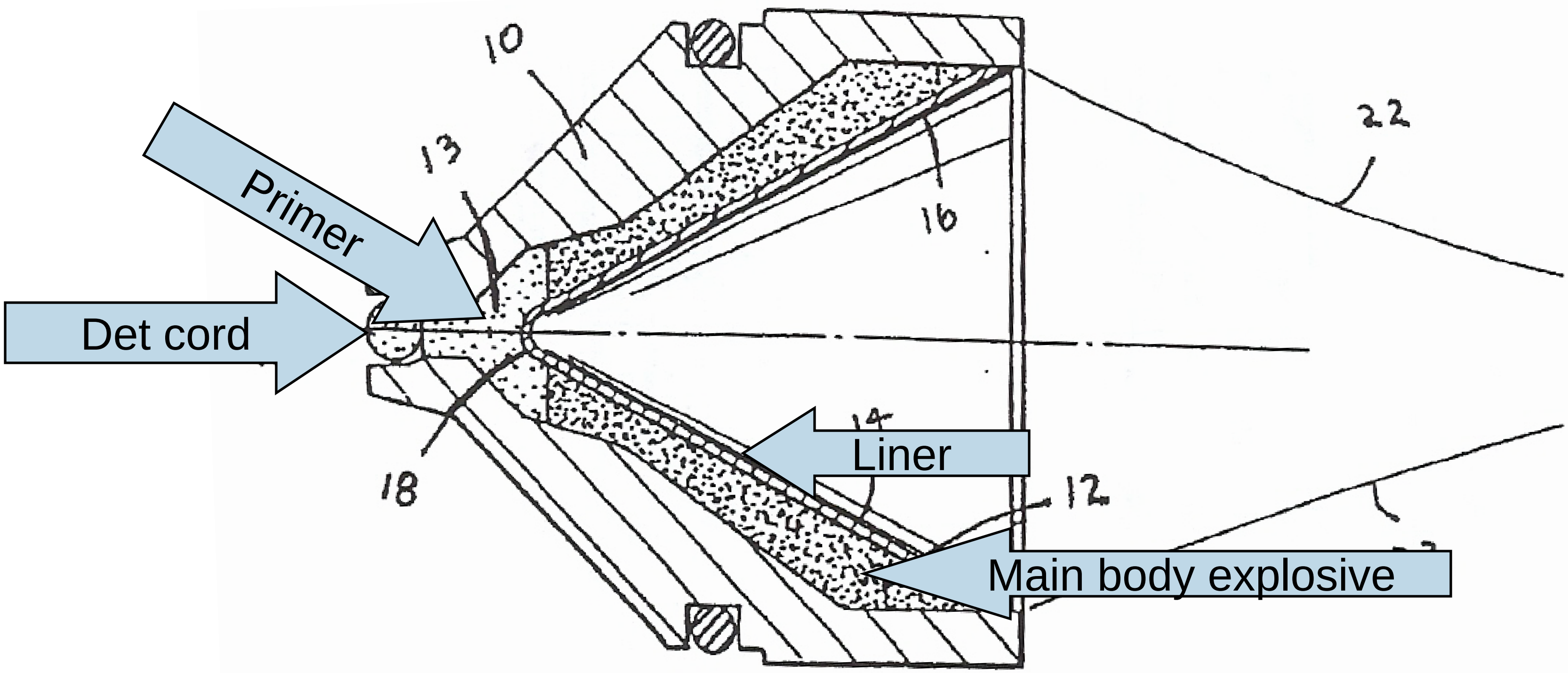
Compound	Impact Sensitivity (cm)	BAM Friction Sensitivity (N)
NONA	20-25	300
RDX	32	120
PETN	17	60
Tetryl	26	350



- EFI image: Barker, J.M. “Exploding foil initiator using a thermally stable secondary explosive” U.S. Patent # 5,431,104, 2002.

NONA uses

- Shaped charges for downhole well applications (oil and gas industry)
- NONA can be used in the primer and/or the main body explosive due to its high thermal stability and its ease of initiation.



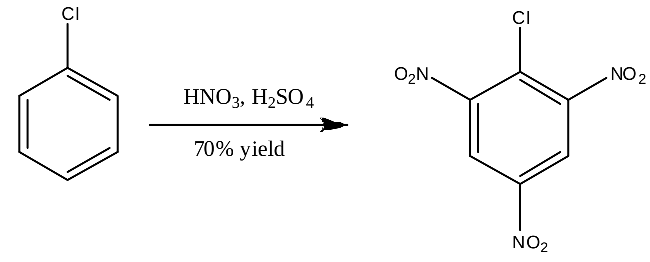
- Yang, W. et al "High Temperature Explosives for Downhole Well Applications" U.S. Patent Application Publication # US 2002/0129940 A1, 2002.

Program Objectives

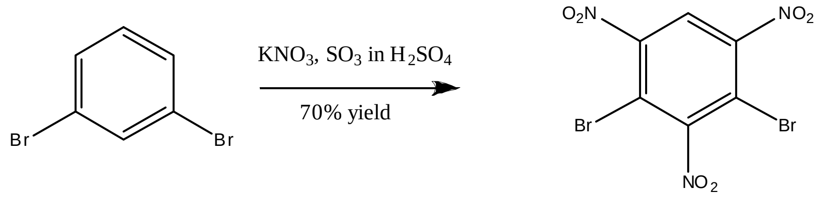
- Develop a process that can produce 1-2 lbs/month of NONA in HSAAP lab facilities
- Develop a process that can be scaled to produce a minimum of 10-20 lbs/month of NONA with minimal infrastructure cost to OSI
- Keep cost competitive!

Original NONA synthesis

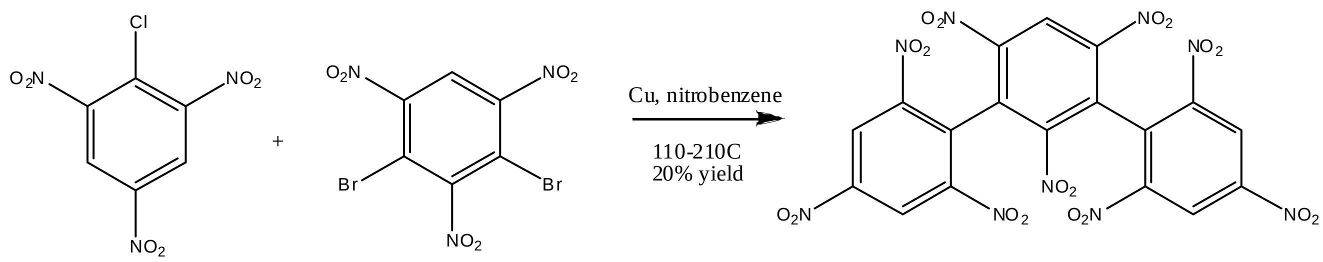
- Picryl chloride and styphnyl bromide are made through harsh nitrations
- Recrystallizations required
- Final step consists of Ullmann coupling in inert solvent(s) at high temperatures.
- Patent method # 3,755,471 (Dacons, 1973)



picryl chloride



SB

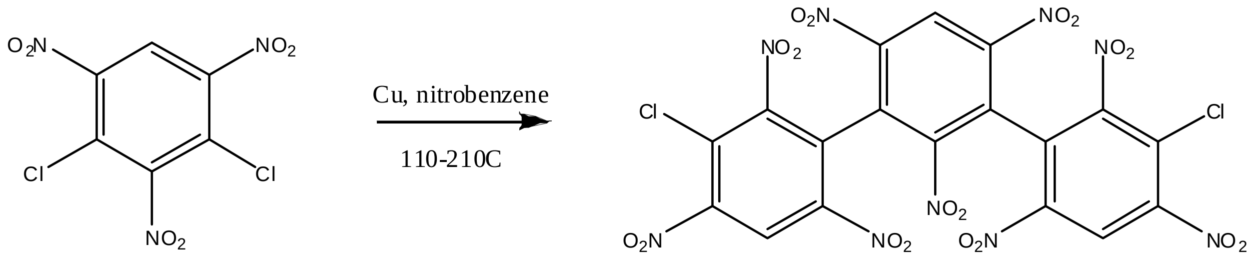


NONA

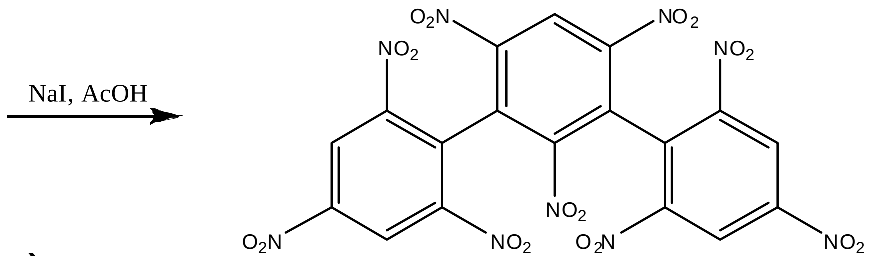
$C_{18}H_5N_9O_{18}$
Mol. Wt.: 635.28

Modified NONA Synthesis

- Sitzmann, M.E. “Method for making nonanitroterphenyl” U.S. Patent # 6,476,280 B1, 2002.



- Styphnyl chloride is homocoupled in Ullmann coupling to produce di-halo-NONA (and biphenyl and quaterphenyl, etc).



NONA

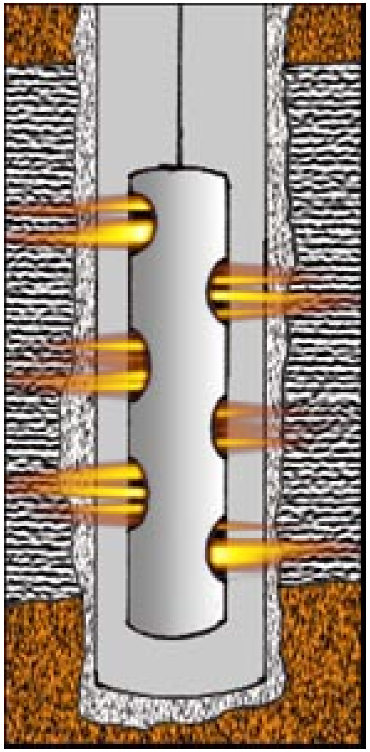
- Resulting material is dehalogenated in final step with iodide source under acidic conditions.
- Terphenyl material can be isolated before or after last step.
- Advantage: only one organic starting material required.

Progress

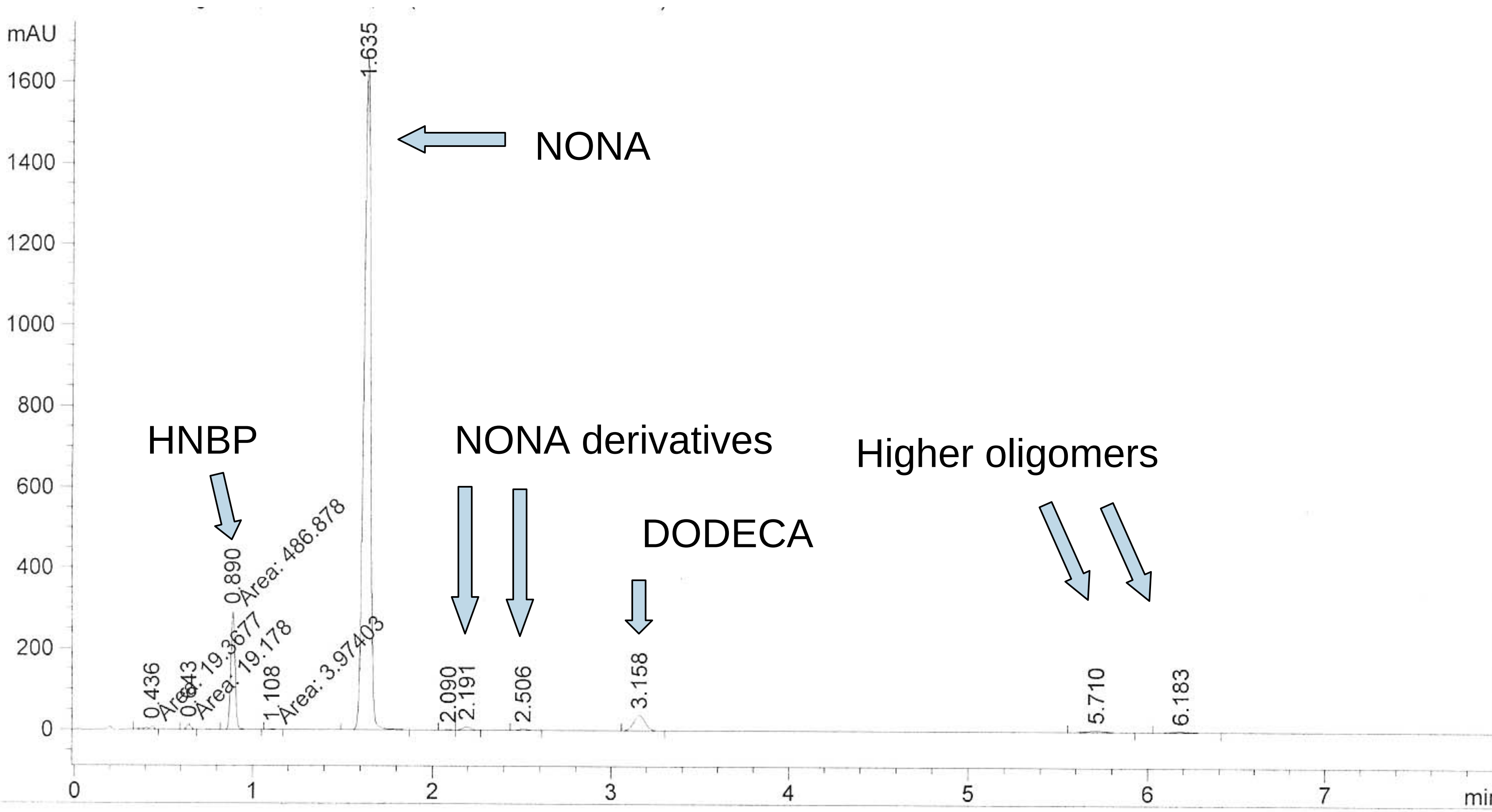
- We have synthesized NONA by the conventional route.
- We now have (and are using) a novel route to produce NONA.
- We are also exploring other, more novel routes to make NONA.

Novel Route Highlights

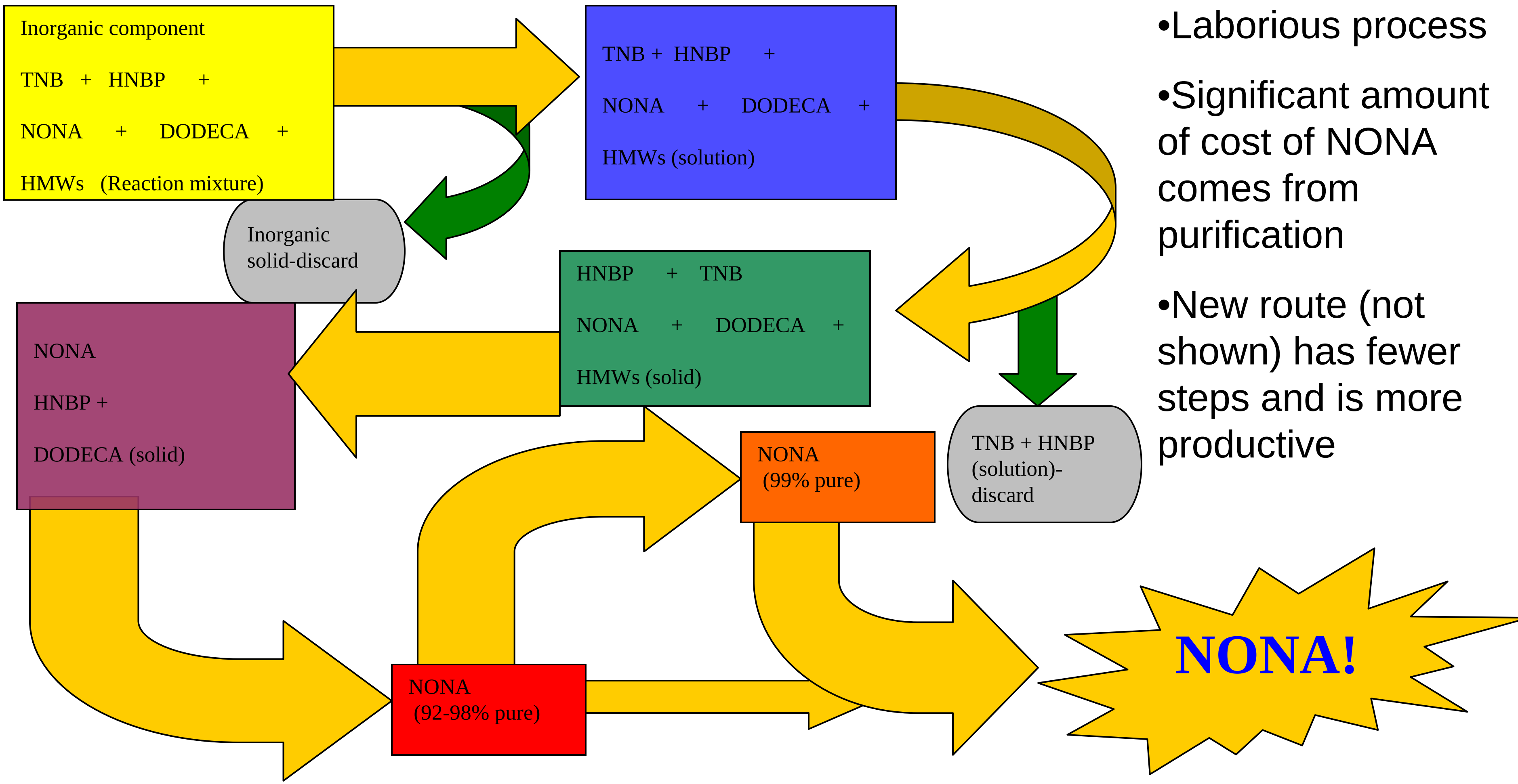
- Lower temperatures required for entire synthetic route
- Scalable on Holston’s infrastructure
- Simpler purification
  - Less solvents (and corresponding waste)
  - Fewer steps
  - Less labor intensive
- Higher yielding route
  - Our yield increased >75%
- Competitive cost



Crude NONA-HPLC analysis



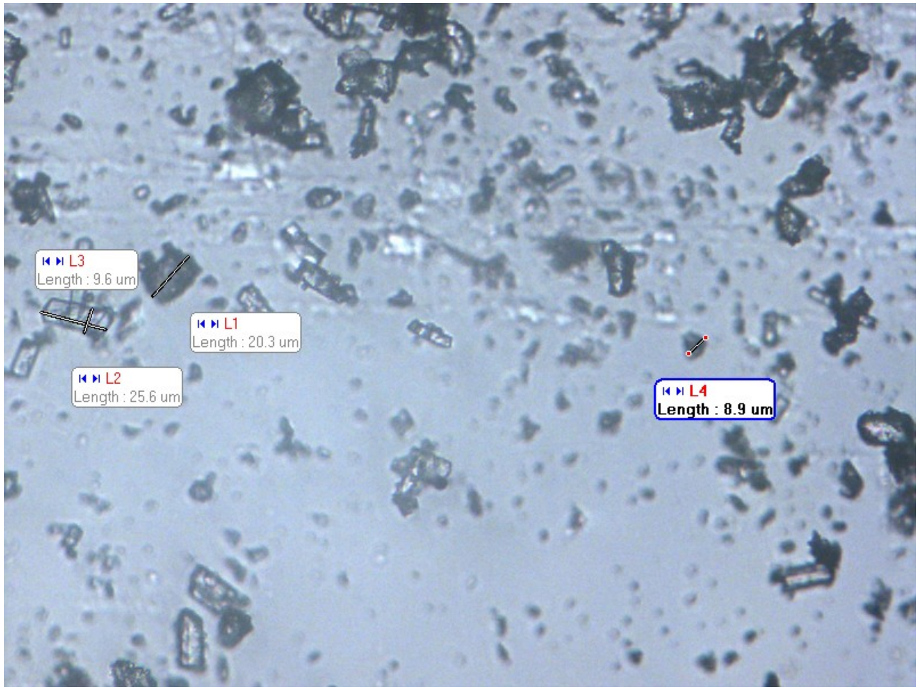
Purification of NONA-old route

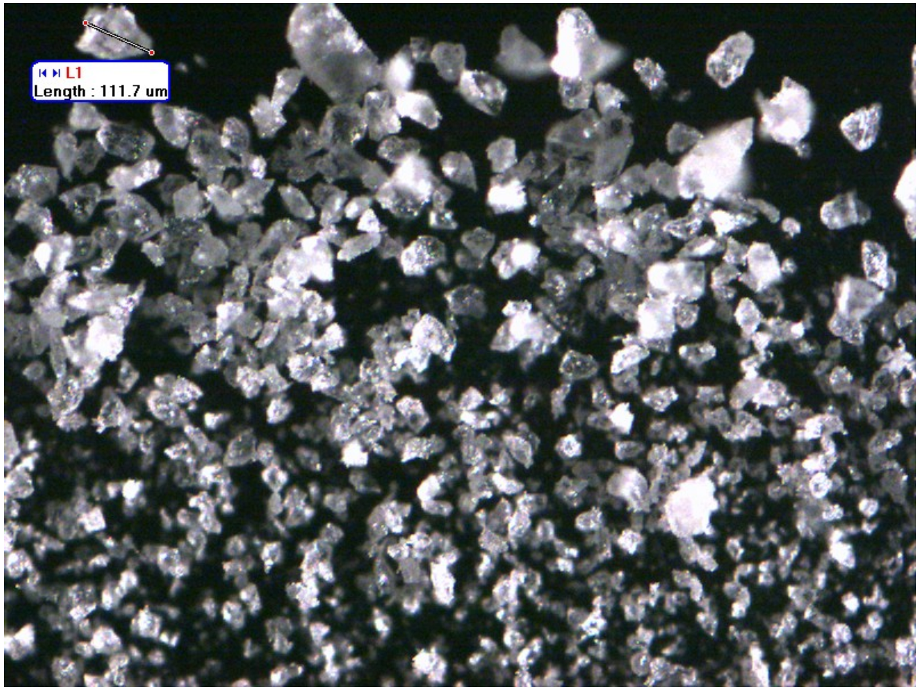


- Laborious process
- Significant amount of cost of NONA comes from purification
- New route (not shown) has fewer steps and is more productive

NONA Particle Size Modification

- Various solvent/antisolvent combinations were evaluated.
- Dissolution in hot solvent and addition of water or IPA affords 15-20 micron material.
- Addition of NONA solution to water or IPA affords <5 micron material.

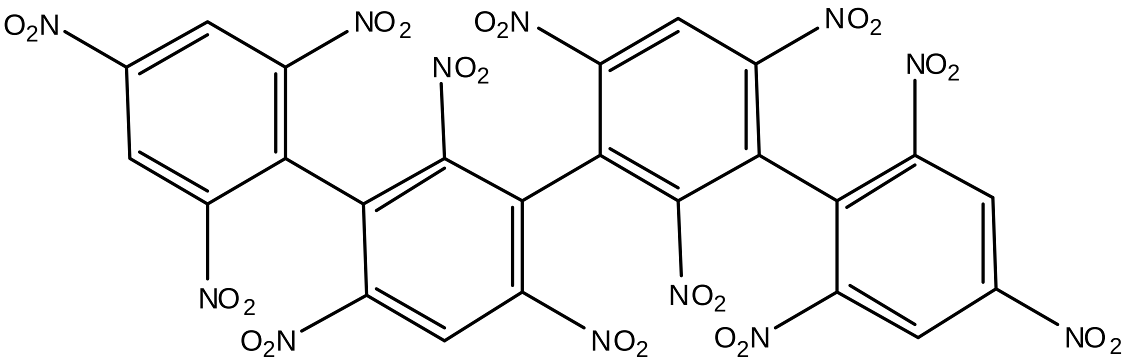




Conclusions

- OSI's novel synthetic route to make NONA should be scalable with little infrastructure cost (still evaluating)
- We are currently producing 1-2 lbs/month of NONA
- We are planning to make larger quantities (10-20 lbs/month) in FY10
- We are also evaluating the manufacture and properties of DODECA, the 4-ring analog of NONA.

DODECA



Acknowledgments

- BAE Systems, HSAAP
  - Mr. Jean Fleischer (the real NONA maker)
  - Mr. Jim Owens
  - Mr. Jim Haynes
  - Ms. Kelly Guntrum
  - Mrs. Lisa Hale