ETPE ManTech Program

Presented at:

2004 Insensitive Munitions and Energetic Materials Technology Symposium

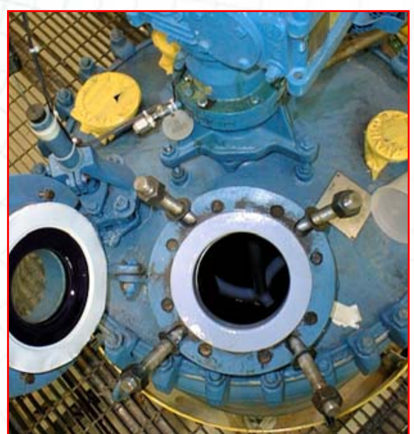
San Francisco, CA

16 November 2004

R. S. Hamilton, V. E. Mancini, A. J. Sanderson

ATK Thiokol Inc. Giving Direction to New Ideas
PEOPLE...PRODUCTS...PERFORMANCE

ATK
ALLIANT TECHSYSTEMS
ATK THIOKOL INC.

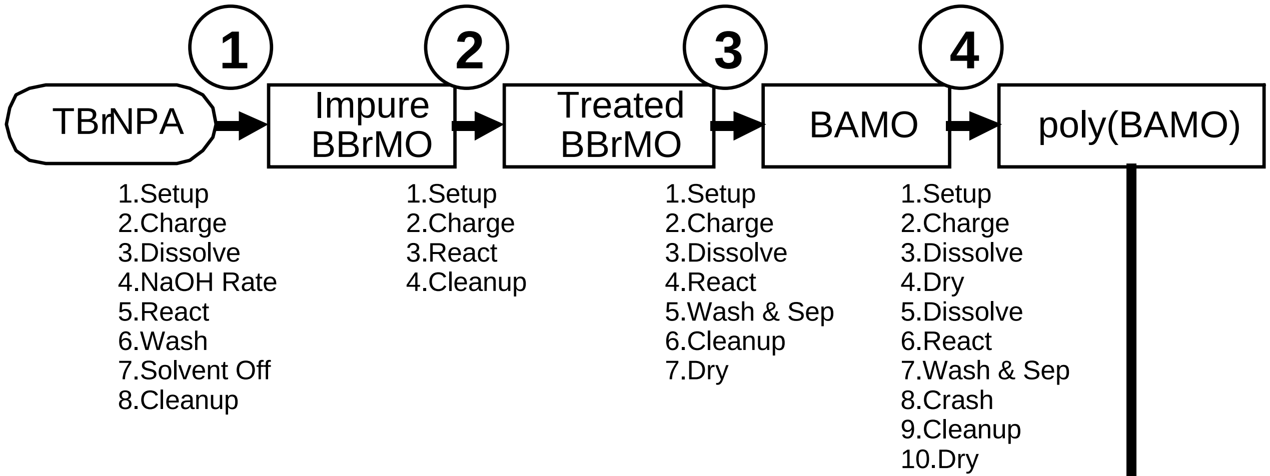


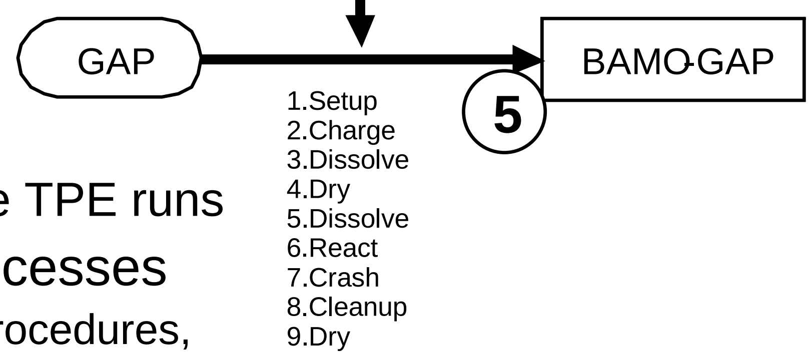
040340

Overview

- Energetic thermoplastic elastomers (ETPEs) are attractive binder systems for advanced gun propellant formulations
  - future utilization of ETPEs in demonstration and pre-production programs will require lower cost production methods than currently available and increased capacity of existing facilities
- ATK Thiokol in conjunction with the US Army Mantech Office has embarked on a program to increase the availability of ETPE materials and at the same time reduce costs
  - Double current production capacity to >2,500 kg/yr
  - Decrease cost by 25%
- Initial efforts have been divided into three tasks focused on the production of BAMO-GAP TPE
  - Construction of a process cost model based on pilot scale data generated from past manufacturing
  - Synthesis studies to develop improved processes that have the maximum effect on reducing cost and increasing production rate and production capacity
  - Demonstration of the improved processes at the pilot scale

Process Cost Model for BAMO-GAP



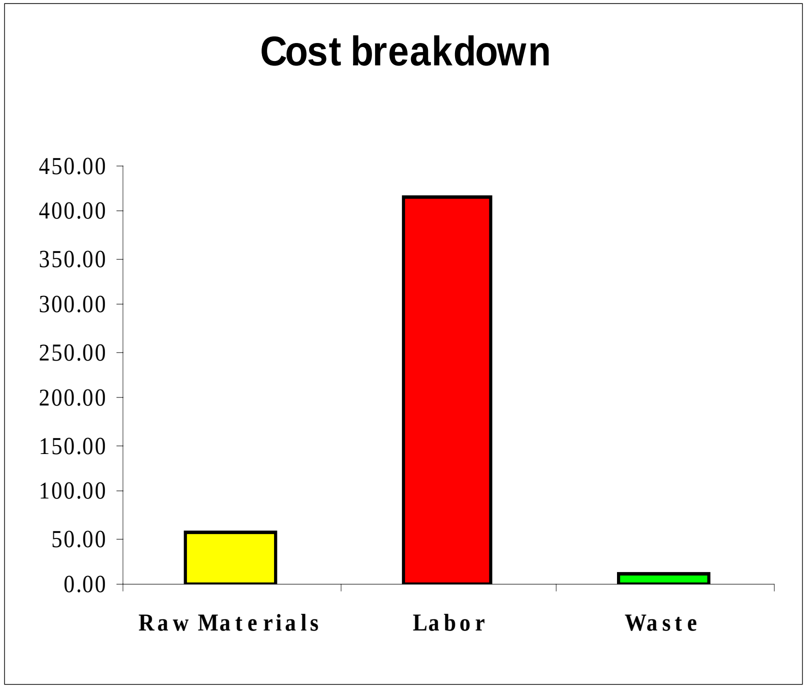


- Included all process costs
  - Materials, waste, labor
  - Based on data from previous pilot scale TPE runs
- Wanted ability to compare different processes
  - Allow for different reaction times, work-up procedures, equipment setup
  - Allow for different impurity levels
  - Visibility of changes in reactor loading
- Used spreadsheet with each process on a separate sheet

1 - ring closure
2 - purification
3 - azidation
4 - polymerization
5 - linking

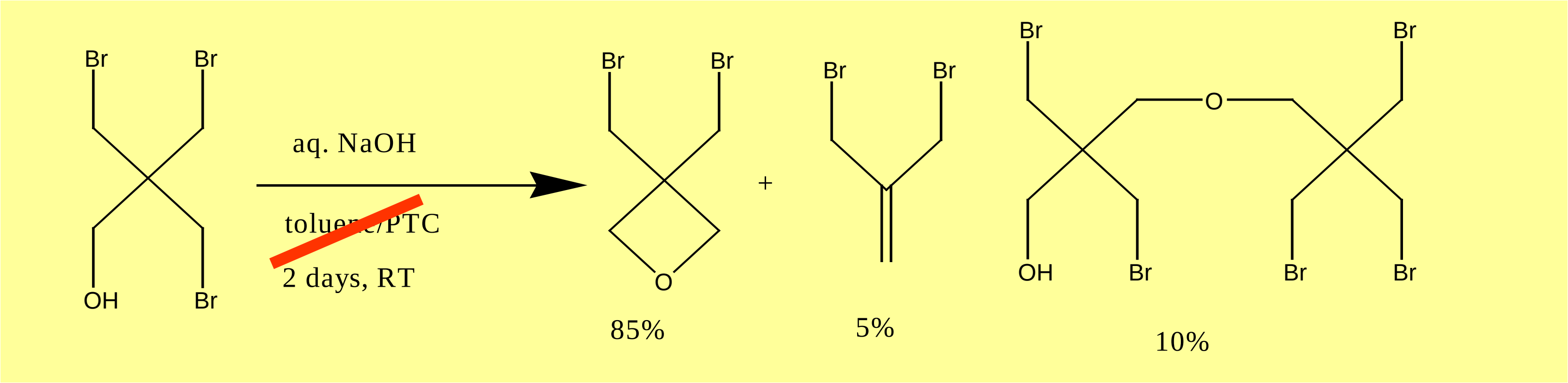
Model Conclusions

- Raw materials and waste are small proportion of cost
  - Scale dependent but valid to ~5 times current scale
- Labor is biggest cost driver - need to increase production per unit labor cost
  - Faster process and/or more product per process
- Relative importance to optimization of different steps in BAMO-GAP TPE production are shown below



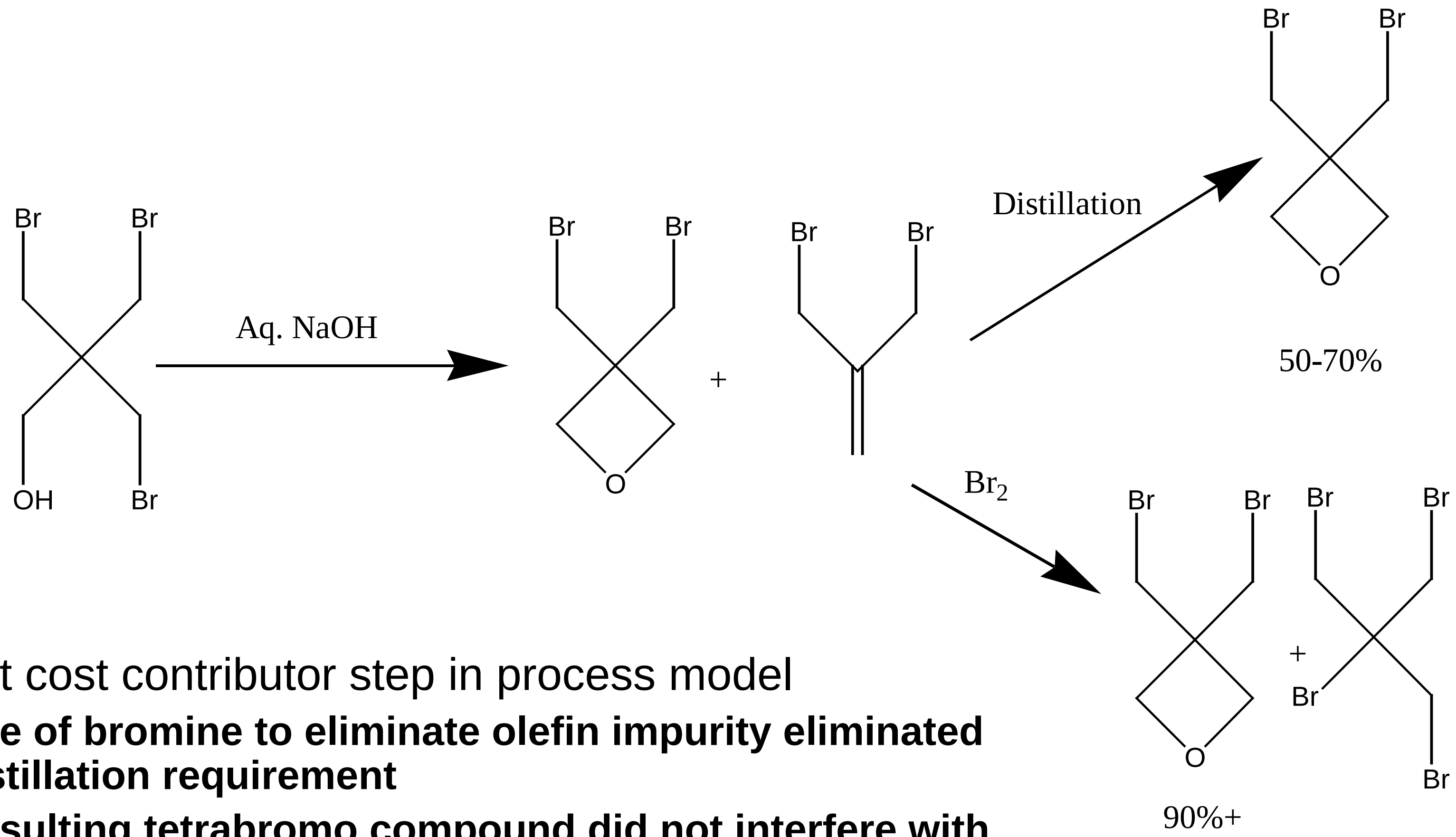
Ring closure >>Azidation > Polymerization >>> Purification

Synthesis – Ring closure



- Key step from model due to slow reaction and low reactor yield (although high reaction yield)
- Eliminated almost all the solvent (including water)
  - Increases reactor loading and reaction rate
- Eliminated phase transfer catalyst (PTC)
  - Surprising cost
  - No longer need to remove after reaction
- Simplified process
  - No change of reaction solution
  - Simplified work-up and product isolation
  - No solvent to remove after reaction
- Is not conducted in main reactor – utilized vertical propellant mixer

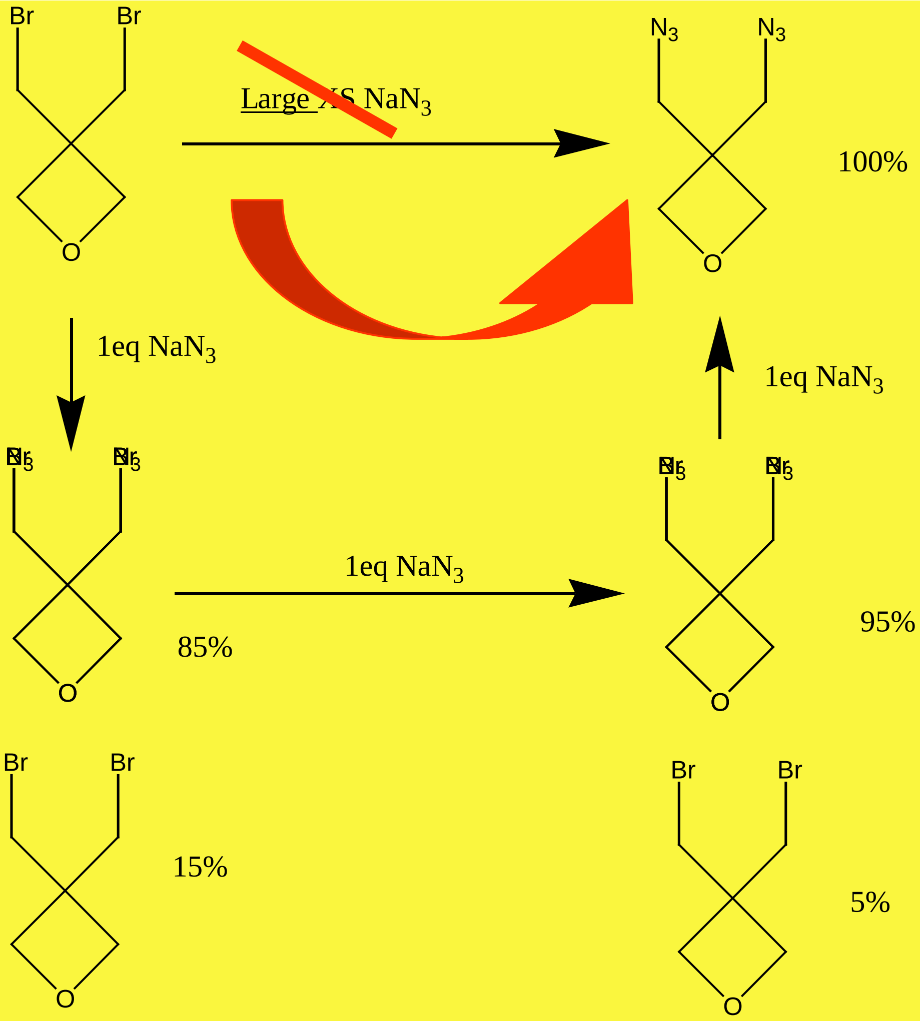
Synthesis – Purification of BBMO



- Lowest cost contributor step in process model
  - **Use of bromine to eliminate olefin impurity eliminated distillation requirement**
  - **Resulting tetrabromo compound did not interfere with subsequent steps**
- Alternate method developed was fractional crystallization of BBMO at low temperature followed by hexanes wash

Synthesis – Azidation of BBMO

- Eliminated organic solvent from reaction
  - Helps reduce materials cost and waste and speeds reaction
- Maximized concentration of sodium azide in aqueous phase
  - excess NaN_3 dissolves as reaction proceeds
- Eliminated need for NaN_3 change out
  - Fewer process steps
- Easier drying step
- Still a key step

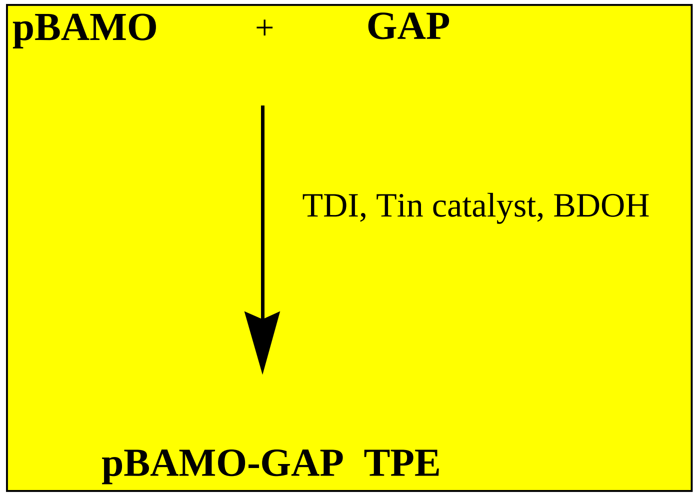


Synthesis – Polymerization of BAMO

$$\text{BAMO} \xrightarrow{\text{DCM, BF}_3\text{, BDO}} \text{HO-pBAMO-OH}$$

- Synthetically most challenging step
  - Need control of reaction to get functionality and molecular weight
- Limited development potential in time-frame due to considerable previous work
- Did find it possible to substantially increase volume yield
  - Both standard process and slow monomer addition process work
  - Additional analysis will determine preferred method
- Selected standard process (U.S. Pat. No. 4,393,199) for pilot plan runs due to past extensive experience with reliability of process

Synthesis – Linking of polyBAMO and GAP



- Considerable work done at kilogram scale
  - Twenty-five 1-kg batches of BAMO-GAP produced for propellant development programs
- Slightly lower reactor yield than traditional procedure but:
  - Significantly less process time
  - Very reproducible
  - Utilized alternate solvent (THF vs DCM) and increased catalyst loading from before (US Patent 6,600,002)

Demonstration of Improved Processes at the Pilot Scale

Lot #	TDI/OH	T (°C)	Mn	Mw	Flow rating (6 is best)	Strength rating (6 is best)
591-03-133	1.000	25	27,123	162,640	1	6
591-03-134	0.975	25	18,204	136,910	5	2
591-03-135	0.995	25	25,000	226,440	2	5
591-03-136	1.000	25	15,765	185,430	4	3
591-03-137	0.975	40	24,807	244,250	3	4
591-03-138	0.965	50	13,419	145,690	6	3-4

- The processes demonstrated in earlier laboratory work (up to 1 kg of final product) were performed in the M-591 pilot plant to give six 25-kg lots of BAMO-GAP TPE
  - Process time and cost of pilot scale reactions exceeded increased capacity goal and met cost reduction goals of program
- Process parameters (TDI/OH ratio and temperature) for the final linking reaction between BAMO and GAP were varied to determine effects on flow and strength of resulting materials
- Optimum combined properties (flow and TPE “strength” were obtained at TDI/OH ratio of 0.975 and reaction temperature of 40°C

Conclusions

- Modeling of the ETPE manufacturing process identified labor as the key element that drives the current cost and limits throughput
- Laboratory studies identified process changes that allowed for fewer steps in each part of the process and allowed for greater reactor loading
- Pilot plant demonstration of the improved process was validated during six runs to produce 25 kg of material per run
- Improvements in the manufacturing process for BAMO-GAP TPE will allow production of >2,500 kg of material per annum in the existing facilities at the Promontory campus of ATK Thiokol, exceeding the program goal and providing sufficient material for next phase of ETPE-based advanced gun propellant development
- Cost reduction goal of 25% for program was achieved

Acknowledgement

- Grateful acknowledgment is made of financial support of this work by the U. S. Army Research Development and Engineering Center at Picatinny Arsenal