AFNOL SYNTHESIS

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DEVELOPMENT DIVISION

APRIL - JUNE 1971
SANL 804-001

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under
U. S. GOVERNMENT Contract DA-11-173-AMC-487 (A)
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Improved methods of AFNOL synthesis to provide useful quantities, e.g., for the Formulation Facility to produce test pieces.

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Section B
AFNOL SYNTHESIS

ABSTRACT

A new method was developed for the chlorination of 4,4-dinitropimelic acid with phosphorus pentachloride using a Soxhlet extraction apparatus as the addition vessel. The acid used for the experiments was that reclaimed from the purification of the crude acid chloride of 4,4-dinitropimelic acid supplied by LRL.

The synthesis of FEFO plasticized AFNOL has been scaled up to a nominal 30-pound batch. Small batches and cure tests were run prior to the scale up.

The cure rate of the AFNOL system was followed by infrared spectrophotometry. The temperature range of 40 to 100°C was studied using the hot stage attachment to the infrared spectrophotometer.

DISCUSSION

CHLORINATION OF 4,4-DINITROPIMELIC ACID

The reaction was run in a Soxhlet extraction apparatus using a 500 ml receiver. Stirring was done magnetically and the heating with an electrical heating mantle. The 4,4-dinitropimelic acid (22.7 g) was slurried with 160 ml of carbon tetrachloride in the extraction thimble. The phosphorus pentachloride (45.4 g) was placed in the extraction thimble. The carbon tetrachloride was refluxed through the thimble thereby causing a slow addition of phosphorus pentachloride to the reaction vessel. After four hours the solution was clear. The extraction receiver was then fitted with a vacuum distillation assembly. The volume was then reduced to less than 50 ml by distillation at which time solids were present. The contents of the extraction receiver were then cooled to 50°C and poured into 150 ml of the stirring petroleum ether. The product was removed by filtration, and washed with three 50-ml portions of petroleum ether.

The yield of 4,4-dinitropimyl chloride (DNPC1) was 21.5 g (82.7% theory) and had a melting range of 54 to 55°C.

The DNPC1 from the above reaction was converted to FEFO-plasticized AFNOL prepolymer. Subsequent cure tests on this product were successful.

The advantage of this reaction method is that it allows the slow addition of phosphorus pentachloride to the refluxing system in a solution form. The reactants are kept dry during addition and the reflux is not interrupted.
PURIFICATION OF 4,4-DINITROPIMYL CHLORIDE

The crude acid chloride received from LRL was purified by extracting the desired product from the carbon tetrachloride insoluble impurities. The extractions were run in three Soxhlet extractors using 100 g loads in fritted glass filtering thimbles. About 0.5% phosphorus pentachloride was added to each thimble in order to keep the system chloride rich.

The extracts were poured into two volumes of petroleum ether. The product was filtered and dried. The yield was approximately 80% (theor.) of a light brown-yellow product. This product was then recrystallized from ethylene dichloride. Difficulty was encountered in reclaiming a solid product from this solution. Recrystallization from carbon tetrachloride was found to be preferable.

The carbon tetrachloride insolubles from the extraction and residues from the evaporation of recrystallization solvents were combined. This product was hydrolyzed giving a product predominantly 4,4-dinitropimelic acid. A sample of this material, recrystallized from boiling water, was carried through the usual reaction scheme to produce FEFO-loaded AFNOL which passed all cure tests.

PILOT BATCH FROM PURIFIED DNPCl

The reactions required to produce approximately 350 g of FEFO-plasticized AFNOL were run on the DNPCl purified by the extraction method. The procedure used was the same as will be described for the nominal 30-pound batch.

The reactants and products for both esterifications are shown below.

First Esterification

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNPCl</td>
<td>30.15 g</td>
</tr>
<tr>
<td>DINOL Hydrate</td>
<td>25.24 g</td>
</tr>
<tr>
<td>Hydrogen Chloride evolved</td>
<td>5.19 g</td>
</tr>
<tr>
<td>Prepolymer yield</td>
<td>49.20 g</td>
</tr>
</tbody>
</table>

Second Esterification

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepolymer</td>
<td>49.20 g</td>
</tr>
<tr>
<td>1,1,1-Trimethylolpropane</td>
<td>5.35 g</td>
</tr>
<tr>
<td>Ethylene Dichloride</td>
<td>450.20 g</td>
</tr>
<tr>
<td>FEFO</td>
<td>305.27 g</td>
</tr>
</tbody>
</table>

The ethylene dichloride was removed by distillation with final traces removed on the rotary drum evaporator. The sample was split with a portion sent to the Formulation Facility for conversion to ECX cylinders and the remaining portion was cured as FEFO plasticized AFNOL.
The ECX samples produced by the Formulation Facility were cured for 40 hours at 65°C. The sample had a Shore A durometer reading of 70 to 75. It was slightly off-white, firm and showed very little signs of plasticizer migration. The FEFO-plasticized AFNOL samples were cured at 80°C for 18 hours after which time they were firm and bubble free. One of the FEFO-plasticized AFNOL cure test samples and the ECX sample were held at 65°C for an additional 15 days with no change in properties being observed.

**Nominal 30-Pound FEFO Plasticized AFNOL Batch**

The starting DNPCl was the material reclaimed by the extraction method previously described. The DINOL used in the first esterification was an Aerojet product which was used without further purification.

The reaction was run in a 5-liter, 5-neck, round bottom flask fitted with mechanical stirring, a nitrogen purge, and a reflux condenser. A water trap was attached to the condenser to monitor evolution of hydrogen chloride. The heating was accomplished by a constant temperature ethylene glycol bath.

DINOL (1236 g) was melted in the reaction flask with dry nitrogen being passed over it for two hours to remove the water of hydration. The DNPCl (1357 g) was added in four batches over a two-hour period. After each addition, the reaction was stirred under a nitrogen purge until excessive foaming subsided.

The hydrogen chloride evolved was trapped in a water trap and titrated with 10N sodium hydroxide. The maximum rate of evolution was reached in about 30 minutes after the first addition. This rate corresponded to 33% reaction completion per hour. After 20 hours this rate was less than 2% per hour. At this stage of the reaction, 1 liter of ethylene dichloride was added and brought to reflux in order to clean out the walls of the reaction vessel.

The second esterification was a solution reaction in ethylene dichloride involving the reaction product from above and 1,1,1-trimethylolpropane (TMP). The plasticizer (FEFO) was added during this esterification. The reaction was run in a 50-liter glass reaction vessel fitted with a reflux condenser, nitrogen purge, electrical heating mantle, mechanical stirrer and a vacuum take-off. The product from the previous esterification was added to the 50-liter vessel and 2 liters of ethylene dichloride were used to wash out the flask. The wash was also added to the 50-liter vessel. TMP (240 g) and 29 kg 1:1 by weight FEFO in ethylene dichloride were then added. The reaction solution was brought to reflux (~80°C) for 20 hours. At this time the hydrogen chloride evolution indicated that the reaction rate was less than 0.1% per hour. The ethylene dichloride was removed by distillation at a reduced pressure with a slight nitrogen purge. Approximately 12 liters of product containing some ethylene dichloride was isolated.

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*aerojet general corporation.*
then filtered through a Celite bed and sent to the Synthesis Facility for further removal of ethylene dichloride.

RATE OF CURE - THIN FILMS

The rate of cure for thin films of the plasticized prepolymer was studied by following the decrease in absorbance of the 4.35μ band in the infrared spectral region. This band was attributed to the isocyanate functional group in the curing agent, hexamethylenediisocyanate (HMDI). A Beckman IR-12 infrared spectrophotometer fitted with a RIIC hot stage attachment was used to monitor the loss of absorbance.

The values used for plotting the rate curves were the ratios of a weak absorbance arising from the skeletal chain of the polymer to the absorbance attributed to the isocyanate group. Fig. 1 shows the plots of these ratios against time at several temperatures between 40 and 100°C. The curves are from the best second degree polynomials. All curves were adjusted to intersect at the origin.

FUTURE WORK; COMMENTS; CONCLUSIONS

The nominal 30-pound batch of plasticized AFNOL will be furnished to the Formulation Facility for further processing. Sufficient DNPCI is on hand to produce approximately 25 pounds of plasticized AFNOL. An additional several pounds of 4,4-dinitropimelic acid are also available.
Fig. 1. AFNOL Cure Rates
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