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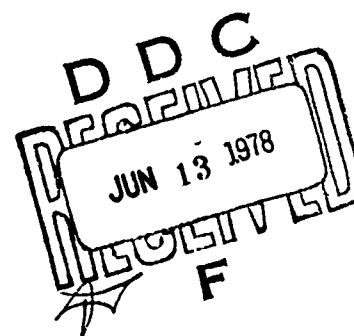
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Polymeric Binders Which Reversibly Dissociate at Elevated Temperatures

by
Ronald A. Henry
Eugene C. Martin
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Research Department

MAY 1978

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FOREWORD

The Naval Sea Systems Command for several years has supported various programs related to pollution abatement. One phase of this work has been concerned with easier or better ways to remove the explosive charge from demilitarized ordnance items; special emphasis has been placed on less-polluting or non-polluting methods. The ultimate method would be one which would permit recovery and re-use of all of the explosive ingredients, either separately or as the mixed formulation. This report describes one approach to accomplishing the last objective, namely, the development of a polymeric binder system for PBX which cures under one set of conditions, reversibly dissociates with liquefaction at a higher temperature, permitting removal of the explosive charge, then re-cures again under the initial conditions.

This work was supported during the period July 1975 through September 1977 under Task Area No. SF53354316.

This report was reviewed for technical accuracy by Russell Reed and William P. Norris.

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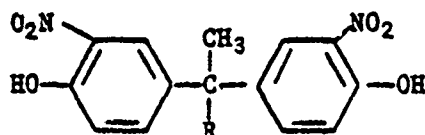
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(U) *Polymeric Binders Which Reversibly Dissociate at Elevated Temperatures*, by Ronald A. Henry, Eugene C. Martin, and Warren J. Murbach. China Lake, Calif., Naval Weapons Center, May 1978. 60 pp. (NWC TP 5995, publication UNCLASSIFIED.)

(U) The synthesis of polyurethane binders, which reversibly dissociate into liquid prepolymers and/or comonomers when heated to 140-150°C and which re-cure to polymer after several days at 25°C, is described. The initial polymers were based on the catalyzed (dibutyltin dilaurate) condensation of a diisocyanate and dinitro-bis-phenol-A (R = CH₃) or dinitro-bis-phenol-B (R = C₂H₅).



The main disadvantage of these latter two compounds is their very poor solubility in either the usual diisocyanates or the common ester plasticizers used in PBX binders. To overcome this shortcoming, dinitro-bis-phenols were prepared in which R was either C₆H₁₃ or C₇H₁₅. These compounds are very viscous liquids which crystallize only with difficulty; more importantly, both are soluble in the usual diisocyanates and plasticizers at ambient temperature. Equimolar mixtures of either the C-8 or the C-9 dinitro-bis-phenol with DDI (no catalyst) remain fluid at 25°C for at least four weeks. When catalyst is added, cure is effected after one to two weeks at ambient, or one to two days at 55-60°C; clear resins are formed.

(U) Other approaches for capping di-carboxylic acid, diols and diisocyanates, so as to have ortho-nitro phenolic end-groups in the prepolymers, have been examined. To date, none appears to be significantly better or to offer advantages over the procedure outlined above.

(U) Methods for making the necessary bis-phenol derivatives in 85 to 90% yield and for their conversion to the desired ortho-dinitro-bis-phenols, also in 85 to 90% yield, have been defined.

(U) Another unique polyurethane which also undergoes reversible dissociation at 140 to 150°C, then re-cures at 25°C, has been made from DDI and 2,5-dihydroxy-2,5-bis-trifluoromethyl-1,1,1,6,6,6-hexafluorohexane.

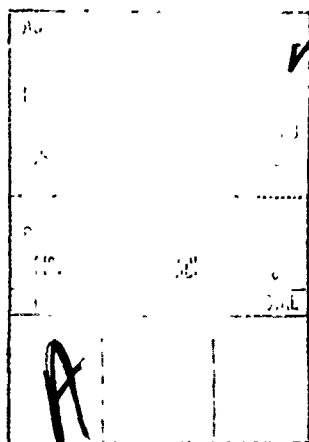
(U) Polymeric binders, which have bonds other than urethane linkages and which might still undergo reversible dissociation have been briefly examined; but for one reason or another the objective was not realized.

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INTRODUCTION

Plastic-bonded explosives (PBX), which utilize crosslinked thermosetting polymers as binders, have several well established advantages: improved and controllable physical properties, improved shock resistance, high impact strength, usable above the usual upper service temperature limit of melt-cast explosives, potential use as structural components, etc. Some limitations include, 1) a finite pot-life in which the slurry mix has manageable viscosity and pour characteristics, 2) inability to use or recycle material which has either cured completely or even cured partially if its viscosity does not permit void-free casting, and 3) difficulty in removing cured PBX from ordnance. Potential advantages of a polymeric binder which would reversibly dissociate into liquid prepolymers or comonomers at temperatures in the range 100-150°C for use in PBX formulations are: 1) an extended (or ideally infinite) pot-life during mixing and formulation, 2) reduced waste since scrap or recovered explosive could be recycled back to the mixing kettle, 3) desensitization of explosive by removal of heat from hot-spots (endothermic dissociation),* 4) possible use of dense, energetic comonomers as curing agents, and 5) easier removal of explosive from demilitarized ordnance.

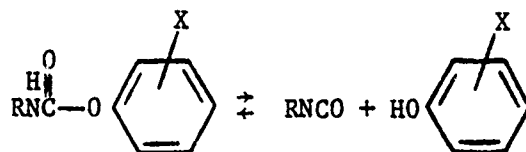
A variety of chemical compounds are known to dissociate reversibly at elevated temperatures or near their melting points. Some of these compounds have found commercial utilization because of this property. The following systems are typical, but by no means exhaust the possibilities. It should also be noted that several of the systems described below can be cured at or near ambient temperature.

BLOCKED ISOCYANATES

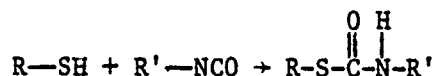
This system would include isocyanate dimers, urethanes, ureas, biurets, etc. The blocking of isocyanate groups has found commercial utilization in single component urethanes used primarily for coatings applications. In order to meet the requirements, materials must be used which are capable of regenerating the free isocyanate on heating and will not undergo undesirable side reactions. The most widely used

* See Appendix A for an extension of this concept.

blocked isocyanates are urethanes derived from phenols.¹ As would be

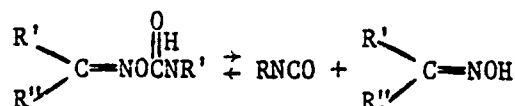


expected, steric as well as electronic factors influence the rate and extent with which a urethane bond is dissociated. This type of de-blocking is also subject to mild catalysis such as amine salts of organic acids² which permit deblocking at lower temperatures. Systems other than phenols can also be used.³ For example, a liquid prepolymer terminated by mercaptan groups will react at room temperature with a diisocyanate as follows:



When this material is heated to approximately 160°C it will dissociate to the free isocyanate and mercaptan.

Oximes derived from various ketones have been employed as isocyanate blocking groups.⁴



As an example, the bis-urethane made from dimer diisocyanate (DDI) and methylethyl ketone oxime is offered commercially as a material which regenerates the diisocyanate when heated to about 150°C.

¹ Z. W. Wicks, Jr. "Block Isocyanates," *Progress in Organic Coatings*, Vol. 3 (1975), pp. 73-99. Also see G. R. Griffin and L. J. Willwerth, "The Thermal Dissociation of Blocked Toluene Diisocyanates," *Ind. Eng. Chem.*, Vol. 1 (1962), p. 265.

² W. Bunge, K. H. Mielke, and F. Moller. *Chem. Abstract* 54, 1926g (1960). Masked Polyisocyanates Having Low Cleavage Temperatures. 12 May 1959. U. S. Patent 2,886,555. (To Farbenfabriken Bayer Akt.-Ges.).

³ S. Peterson. "Niedermolekulare Umsetzungsprodukte Aliphatischer Diisocyanate," *Ann. Chem. (Leipzig)*, Vol. 562 (1949), p. 205

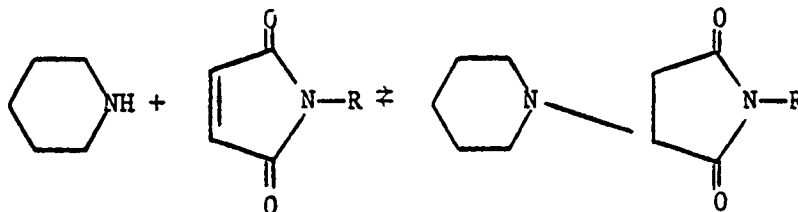
⁴ A. W. Levine and J. Fech, Jr. "The Chemistry of Blocked Isocyanates," *J. Org. Chem.*, Vol. 37 (1972), p. 1500; Vol. 37 (1972), p. 2458.

The isocyanate dimer (or uretidione) linkage⁵ and the urea linkage are other groups that will dissociate at elevated temperatures. Again, catalysts such as triethylphosphine can be used to lower the dissociation temperature.⁶

Isocyanate derivatives of weakly basic amines, such as imidazole, indazole and benzotriazole, exhibit a marked tendency to dissociate at temperatures as low as 80°C to 100°C. With 4,5-diphenylimidazole this dissociation is essentially complete at 110°C.⁷

MALEIMIDE DERIVATIVES

The conjugated double bond of maleimide and its derivatives will not only undergo a Diels-Alder reaction at room temperature with a variety of dienes, but it will also react with other functional groups. Many of these derivatives are stable at ambient temperature; however, when heated, they will dissociate. For purposes of illustration, the piperidinium adducts are sharp melting crystalline compounds and are stable under normal conditions, but decompose to the original components when heated above their melting points.⁸ The general reaction is as follows:



DIELS-ALDER ADDUCTS

Various types of compounds capable of entering a Diels-Alder type reaction can be designed to undergo a retrodienic decomposition. This characteristic is influenced by the configuration of the diene and neighboring substituents. Nitrosobenzene reacts readily with

⁵ B. Taub and C. E. McGinn. *Chem. Abstract* 53, 4106d (1959). "The Chemistry of Isocyanate Dimers and Trimers," *Dyestuffs*, Vol. 42 (1958), p. 263.

⁶ W. Siefkin. "Mono- und Polyisocyanate. IV. Mitteilung über Polyurethane," *Ann. Chem. (Leipzig)*, Vol. 562 (1949), p. 75.

⁷ R. A. Henry and W. M. Dehn. "Aromatic Isocyanates as Reagents for the Identification of Some Heterocyclic Compounds," *J. Am. Chem. Soc.*, Vol. 71 (1949), pp. 2297-2300.

⁸ A. Mustafa and others. "On the Reactivity of the Unsaturated System in N-Arylmaleimides," *J. Org. Chem.*, Vol. 26 (1961), pp. 787-39.

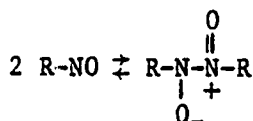
cyclopentadiene at low temperature to form the Diels-Alder adduct. At room temperature, the cycloadduct dissociates into the original reactants. The cycloadduct formed between nitrosobenzene and 1,3-cyclohexadiene is stable at room temperature.⁹

Maleic anhydride, maleimide, and its N-substituted derivatives readily react with cyclopentadiene to form the corresponding endo adduct in a quantitative yield. These compounds, on heating, dissociate into the original components.¹⁰

Diels-Alder adducts of the fulvenes readily undergo retrodienic dissociation. It has been shown that in many cases these adducts are stable only in the solid state.¹¹ It has also been reported that the maleic anhydride adducts of aliphatic fulvenes dissociate more readily than those of the aryl fulvenes.¹²

NITROSO DIMERS

Aliphatic nitroso compounds exist as dimers unless the α -carbon has a strong electron-withdrawing group such as a cyano or halogen group. Likewise, aromatic nitroso compounds will form dimers unless strong electron-withdrawing groups are on the ring. The general reaction for dimer formation is as follows:



These stable nitroso dimers will dissociate into monomeric nitroso compounds when heated in solution or near their melting point; approximately 25 Kcal/mole are required to effect dissociation.¹³

⁹ G. Kresze and G. Shulz. "Additionsreaktionen der Nitrosogruppe-II," *Tetrahedron*, Vol. 12 (1961), p. 7.

¹⁰ E. J. Prill. *Chem. Abstract* 45, 1162e (1951). Maleimide and N-Substituted Derivatives. 3 October 1950. U. S. Patent 2,524,136 (to U. S. Rubber Co.); P. O. Tawney. *Chem. Abstract* 45, 1162i (1951). Maleimide and N-Substituted Derivatives. 3 October 1950. U. S. Patent 2,524,145 (to U. S. Rubber Co.).

¹¹ E. P. Kohler and J. Kable. "The Diels-Alder Reaction in the Fulvene Series," *J. Am. Chem. Soc.*, Vol. 57 (1935), p. 917.

¹² K. Alder and H. F. Rickert. "Zur Kenntnis der Dien-Synthese," *Ber.*, Vol. 70 (1937), p. 1354.

¹³ F. von Keussler and W. Luttke, "Spektroskopische Untersuchungen an Nitrosoverbindungen," *Z. Elektrochem.*, Vol. 63 (1959), p. 614.

APPROACH

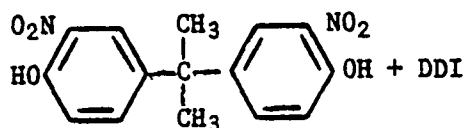
Knowing that there were several different classes of compounds which would undergo reversible thermal dissociation, demonstrating the feasibility of a dissociable binder for PBX formulations involved selecting or preparing prepolymers which could be reacted with appropriate curing agents to generate a polymer with the desired kind of bonds. Several restrictions were placed, however, on the selection process: 1) the monomers, prepolymers or polymers should be commercially or currently available whenever and wherever possible, 2) if required, commercially available materials should be easily and simply modified in order to meet the objectives of the investigation, 3) if new prepolymers or chain-extending agents with two or more suitable functional groups were needed, their synthesis should be based on uncomplicated, high-yield reactions from readily obtainable precursors. In other words, cost and availability were always to be important considerations. Furthermore, the reactants which were selected should not only give liquid components when thermally dissociated in the range 100-150°C but should give: 1) a liquid phase of low viscosity, good wetting properties, etc. needed for easy processing of high-solids, loaded explosive formulations at 25-60°C (or a liquid prepolymer if plasticized suitably), and 2) a polymer with the requisite physical and elastomeric properties over the service range (low T_g , proper stress-strain characteristics). Finally, from a safety standpoint, the components of the reversibly, dissociable binder system should be compatible with the explosive both under storage conditions and at the temperature needed to dissociate bonds and reliquefy the binder.

EXPERIMENTAL

In the following sections are summarized many of the experiments which were performed either to demonstrate the concept of a reversible, dissociable binder or to define systems and conditions for a potentially useful binder once the concept was demonstrated. Pertinent observations and results are included for each experiment. Experiments have also been grouped into related classes of reactions for easier comparison.

Syntheses of various precursors used in the polymer work are given in Appendixes B and C.

DISSOCIABLE POLYURETHANES

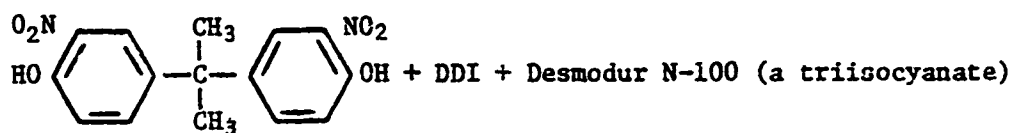


- Mole Ratio: 1:1
 Plasticizer/Solvent: None
 Catalyst: Pyridine (approximately 1%)
 Results: The initially heterogeneous system slowly became homogeneous as the mixture was heated at 100°C for 69 hr; the urethane carbonyl absorption increased, and the isocyanate decreased. However, the condensation was still far from complete and a substantial uretidione carbonyl absorption was also developing.
- Mole Ratio: 1:1
 Plasticizer/Solvent: Tetrahydrofuran (THF) (1 part per part of reactants)
 Catalyst: 1,3-bis(4-pyridyl)propane (2.1% based on weight of reactants)
 Results: After two weeks at ambient temperature only a limited amount of reaction had occurred.
- Mole Ratio: 1:1
 Plasticizer/Solvent: THF (1 part per part of reactants)
 Catalyst: Thermolite #12 (approximately 1%)
 Results: The isocyanate absorption in the infrared spectrum decreased and the urethane carbonyl increased slowly when the homogeneous solution was allowed to stand at ambient temperature. After nine days essentially no further change occurred. The polymer was free of uretidione (absence of homopolymerization of the diisocyanate). When a sample of the polymer, freed of THF, was heated to 150-154°C for 8 min, then quenched, some uretidione was formed.
- Mole Ratio: 1:1
 Plasticizer/Solvent: THF (1 part per part of reactants)
 Catalyst: Dibutyltin dilaurate (Thermolite #12) (approximately 1%)
 Results: After 25 hr at ambient temperature the solvent was removed at pump limit on a rotary evaporator. Sufficient reaction had occurred so that the dinitro-bis-phenol-A no longer crystallized or precipitated from the viscous liquid. Curing

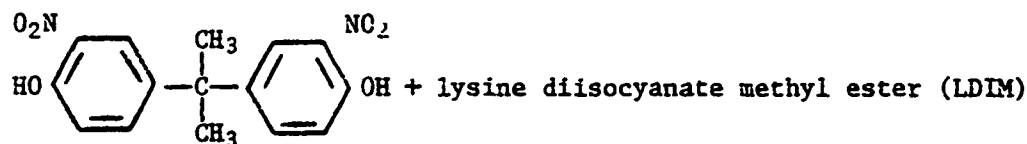
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then continued and was essentially complete in four more days. Upon long standing the initially clear, transparent resin became opaque.

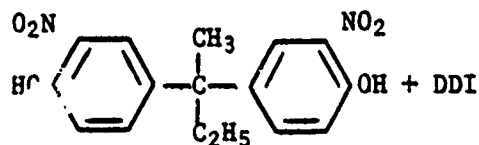
- Mole Ratio: 1:1
 Solvent: THF (1 part/part of reactants necessary in order to have homogeneous solution at 25°C)
 Catalyst: Thermolite #12 (0.7%)
 Plasticizer: Bis-dinitropropyl formal/acetal (BDNPF/A) (20% of binder)
 Results: The condensation was allowed to go to completion (about two weeks at ambient) before the plasticizer was added. Removal of the solvent left a soft homogeneous mass. The presence of the plasticizer did not interfere with the dissociation at 146°C nor with the re-cure after re-cooling to ambient temperature. Upon standing about five months at ambient the system became opaque and heterogeneous.



- Equivalent Ratio: 0.0218:0.02:0019
 Solvent: THF (1 part per part of reactants)
 Catalyst: Thermolite #12 (0.6%)
 Results: Again, about two weeks at 25°C required for cure. Polymer left after solvent was removed appeared to be somewhat harder and tougher than that obtained with DDI above. The binder obtained by plasticizing with 20% of BDNPF/A was heterogeneous.

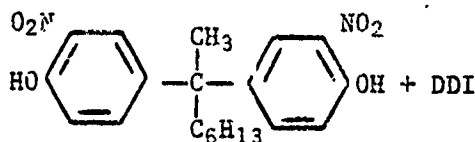


- Mole Ratio: 1:1
 Solvent: THF (1 part per part of reactants)
 Catalyst: Thermolite #12 (1.1%)
 Results: The stoichiometric amount of LDIM was grossly insufficient for dissolving the dinitro-bis-phenol-A. Cure in the THF solution proceeded normally.



Mole Ratio: 1:1
 Plasticizer/Solvent: THF (0.4 part per part of reactants)
 Catalyst: Thermolite #12
 Results: Dinitro-bis-phenyl-B was somewhat soluble in DDI at 25°C; by heating to 70°C a substantial amount dissolved. Upon re-cooling to ambient, it recrystallized. Complete solution was readily attained at 25°C (with a small amount of THF). About two weeks at ambient were required for complete cure. The hard, tough polymer had become opaque after standing 14 months.

Mole Ratio: 1:1
 Plasticizer/Solvent: BDFP/A (17% of binder on weight basis)
 Catalyst: Thermolite #12 (0.5%)
 Results: By warming to 70°C for 2 hr (catalyst not added), a fluid, homogeneous solution was attained. However, some crystallization again occurred upon re-cooling to 25°C. After the catalyst was added and dissolved, the heterogeneous formulation was partially cured at ambient temperature for four days; then the mix was heated with occasional stirring at 68-69°C for 2 hr until homogeneous. Final cure occurred at 25°C. This rubbery binder also became opaque after standing 14 months at room temperature.

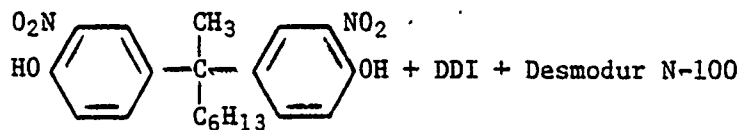


Mole Ratio: 1:1
 Plasticizer/Solvent: None
 Catalyst: Ferric acetylacetonate
 Cure Temperature: Ambient and 56-58°C
 Results: No cure after six weeks at ambient; still a fluid liquid after one week at 56-58°C. Still flowed 5-1/2 months after catalyst added.

Mole Ratio: 1:1
 Plasticizer/Solvent: None
 Catalyst: Triphenylbismuth (0.054 wt %)
 Results: The homogeneous, liquid mixture had an initial viscosity at 25°C of 10.6 Pa·s. It still flowed after six weeks at ambient but did not flow after ten weeks. When heated under dry nitrogen for 1 hr at 139-143°C, the resin melted and remained fluid upon cooling to 25°C; the viscous liquid would still flow after 1 hr, but the tough, tacky resin would not flow after standing overnight.

Mole Ratio: 1:1
 Plasticizer/Solvent: None
 Catalyst: Thermolite #12 (0.2%)
 Cure Temperature: 55-57°C
 Results: After 20 hr at cure temperature, the resin was so viscous that it would barely flow. By way of comparison, a portion of the same catalyzed mixture kept at 25°C still flowed after six days, but not after 11 days. An uncatalyzed mix was very fluid after four weeks.

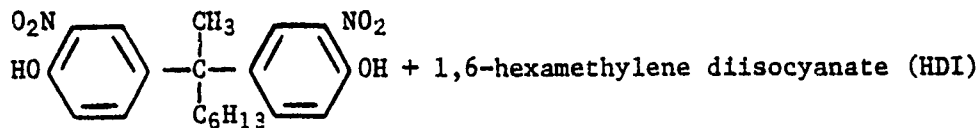
Mole Ratio: 1:1
 Plasticizer/Solvent: Isodecyl pelargonate (IDP), 23.4% (wt basis)
 Catalyst: Thermolite #12 (0.4%)
 Cure Temperature: Ambient
 Results: The mix had an initial viscosity of 3.8 Pa·s. The cured resin was always very soft; even after nine months, it would still flow slowly at 25°C. An uncatalyzed portion of this plasticized blend was still homogeneous and fluid after nine months.



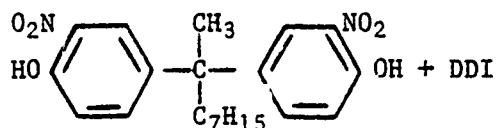
Equivalent Ratio: 0.0296:0.0266:0.00296
 Plasticizer/Solvent: None
 Catalyst: Thermolite #12 (0.33%)
 Cure Temperature: 55-56°C
 Results: The reactants, less catalyst, were mixed overnight at ambient temperature, then for 1 hr at 55°C. Even though the mixture was still heterogeneous, the catalyst was added and thoroughly dispersed. After 24 hr at cure temperature, the resin would barely flow; after 48 hr it was a tough, but heterogeneous, solid.

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Equivalent Ratio: 0.0204;0.0184;0.0204
 Plasticizer/Solvent: IDP (20% weight of binder)
 Catalyst: Thermolite #12 (0.39%)
 Cure Temperature: 55-56°C
 Results: Like the above system, this plasticized system never became homogeneous prior to or during cure. At this level of plasticizer the resin was soft and tacky and cold flowed at ambient temperature.

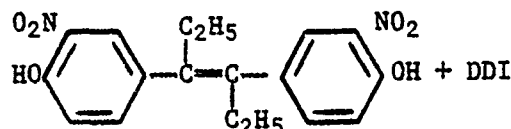


Mole Ratio: 1:1
 Solvent: None
 Catalyst: 0.26% (wt basis) of Thermolite #12
 Cure Temperature: 54-58°C
 Results: The reactants, when warmed to 52-55°C and shaken, very rapidly formed a fluid, homogeneous mix. Curing for 24 hr gave a hard brittle resin. Partial depolymerization by heating to 140-145°C for 15 min yielded a liquid, which was mixed with IDP (19.7% wt basis) and stirred until homogeneous. Upon re-cooling to ambient and allowing re-cure, the system became opaque and heterogeneous.

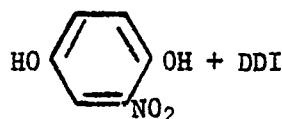


Mole Ratio: 1:1
 Solvent: None
 Catalyst: Thermolite #12 (ca 1% wt basis)
 Cure Temperature: Ambient
 Results: The dinitro-bis-phenol used here was recrystallized solid rather than the viscous liquid product from chromatograph purification. By warming to 50-70°C and swirling, a homogeneous liquid mixture was quickly attained; it remained fluid (no catalyst) with no signs of crystallization for the three days before the catalyst was added. After two weeks the mixture had cured to a soft, tacky resin, similar to that obtained with liquid dinitro-bis-phenol. After 13 months at ambient temperature,

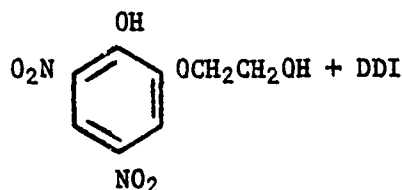
the polymer was still tough and flexible; however, it had become opaque and it was now only partially soluble in THF. The insoluble material was extracted several times with THF, then with acetone, and finally dried. A nitrogen analysis (4.92%) on this insoluble material suggested DDI homopolymer (theoretical N:4.77%). (The calculated nitrogen content of the polyurethane is 5.58%.)



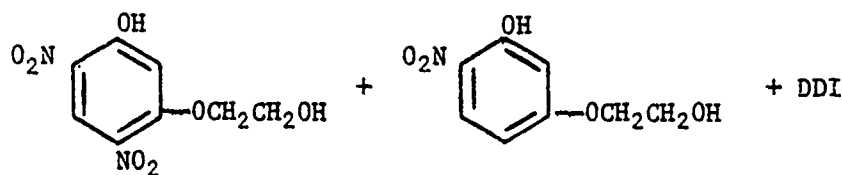
Mole Ratio: 1:1
 Solvent: THF
 Catalyst: Thermolite #12
 Results: Always a heterogeneous system; the DDI homopolymerized after five weeks at 25°C.



Mole Ratio: 1:1
 Solvent: THF (0.36 parts per part of reactants)
 Catalyst: Thermolite #12
 Results: Since the nitrohydroquinone was somewhat soluble in DDI without added THF, only a very small quantity of the latter was needed to furnish a homogeneous system. No reaction occurred in the absence of catalyst after three days at 25°C. Very extensive urethane formation had taken place within 24 hr after the catalyst was added. When cured, the solvent was removed to leave a tough, stretchy polymer. Extensive dissociation (appearance of NCO absorption in infrared spectrum) resulted when the polymer was heated at 145-147°C for 4 min. Re-cure was complete after three days at ambient.

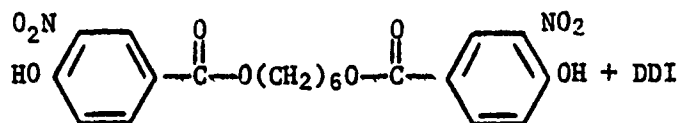


Mole Ratio: 1:1
 Solvent: THF (2.5 parts/1 part of reactants)
 Catalyst: Thermolite #12
 Cure Temperature: Ambient
 Results: Without solvent, the mix was heterogeneous and remained so after almost two weeks at ambient (no catalyst). When fresh reactants were slurried in the indicated amount of solvent (no catalyst), after four days the solution became homogeneous due to urethane formation between the DDI and the primary aliphatic hydroxyl group of the dinitrophenoxy compound. At this point, the addition of catalyst effected further cure involving the phenolic group; after about nine weeks, isocyanate had almost completely disappeared. Removal of the solvent left a soft, tacky polymer. On one occasion, in a supposedly similar experiment, a different behavior was noted. Three days after the catalyst had been added to the homogeneous solution, a new crystalline solid began to form and slowly increased in quantity. It was removed, washed with THF and dried. Some was recrystallized from ethanol, in which it was only sparingly soluble as fine orange needles, m.p. 175-176°C. The infrared spectrum showed urethane carbonyl. The elemental analyses suggest that this could be an intramolecular 1:1 condensation product.

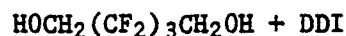


Mole Ratio: 2:1:3
 Solvent: THF
 Catalyst: Thermolite #12
 Results: Almost six weeks at ambient temperature elapsed before the isocyanate was completely reacted. The solvent was removed at 25 mm, first at 25°C, then by heating to 55-60°C, to leave a tacky, red-orange

resin, which had a very low tendency to cold flow and to self-heal at ambient temperature; cuts or scratches persisted for weeks. (The neat reactants did not form a homogeneous mixture even when heated to 75°C.)

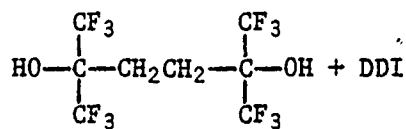


Mole Ratio: 1:1
 Solvent: THF
 Catalyst: Thermolite #12
 Results: Because of the very poor solubility of the diester, a homogeneous system was never attained.



Mole Ratio: 1:1
 Solvent: THF (1 part per part of reactants)
 Catalyst: $\begin{array}{c} \text{CF}_3 \\ | \\ \text{NaOC}-\text{CH}_2\text{CH}_3 \\ | \\ \text{CF}_3 \end{array}$

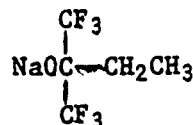
Results: In the absence of the catalyst very little reaction had occurred after 16 hr at 25°C. The reaction was complete within 20 min after adding catalyst. A soft, tacky, colorless resin was formed.



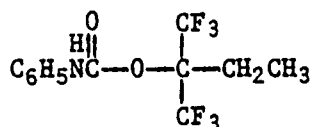
Mole Ratio: 1:1
 Solvent: THF (0.55 part of solvent to 1 part of reactants)
 Catalyst: Thermolite #12 (approximately 1%)
 Results: Almost three months at ambient temperature were required for complete reaction. Removal of solvent left a clear, white, tough, slightly tacky resin. Triethylene diamine (DABCO) was even less effective as a catalyst.

Mole Ratio: 1:1
 Solvent: THF (0.8 part per 1 part of reactant)

Catalyst;



Results: Only about two weeks at ambient temperature elapsed before the isocyanate was completely reacted. When heated to 147-148°C for 2 min this polymer underwent extensive dissociation (appearance of NCO) and liquefied. After 24 hr at ambient, it re-cured to a tough clear resin. The behavior was the same on a second cycle -- heating to 148°C, quenching and allowing to re-cure.

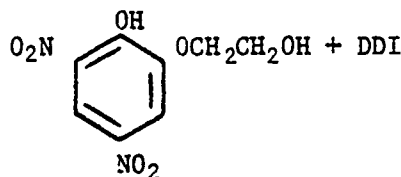


Equivalent amounts of phenylisocyanate and 2-hydroxy-2-trifluoromethyl-1,1,1-trifluorobutane, plus a catalytic amount of Thermolite #12, slowly solidified. After seven weeks the product was recrystallized from n-hexane; m.p. 91-92°C.

Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{F}_6\text{NO}$: F, 36.17; N, 4.44. Found: F, 36.35; N, 4.61.

The same condensation required only about 5 min if 3% of the sodium salt of the fluorinated alcohol was used as the catalyst instead of the Thermolite #12.

END-CAPPING



Mole Ratio: 2:1

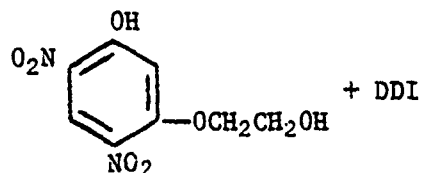
Solvent: THF

Catalyst: Thermolite #12, approximately 1.6%

Results: Based on the infrared spectrum, the isocyanate had completely reacted within 16 hr at 25°C. Removal of the solvent left a bright yellow, waxy, end-capped DDI, m.p. 78-79°C. When another equivalent of DDI was added, a heterogeneous system was

obtained; no change was observed after one week at room temperature. Heating to 67-68°C did not give a homogeneous solution. When heated to 100°C, a liquid mix, which contained some gel, resulted; upon cooling to 25°C, a clear, viscous resin was initially obtained but upon standing it became opaque and heterogeneous.

Several attempts to dissolve this end-capped DDI in plasticizer, in order to get liquid systems suitable for chain-extending, were made. Various levels of BDNPF/A were tested; but even when the prepolymer:plasticizer ratio was 1:1.75, the system was heterogeneous at 25°C, although liquid and homogeneous at 70°C. With an equal weight of di-n-butyl sebacate the mix was homogeneous and liquid at 70°C, but heterogeneous (liquid plus solid) at ambient. The results were similar when an equal weight of dibenzyl sebacate was employed; addition of an equivalent amount of DDI at 70°C did not alter the behavior since crystallization again occurred upon cooling to ambient. Curing of this latter composition was unsatisfactory; the product consisted of soft, crumbly curds.

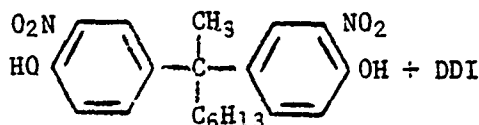


Mole Ratio: 2:1

Solvent: THF

Catalyst: Thermolite #12

Results: Isocyanate had completely reacted within one week at ambient temperature; solution was always homogeneous. Removal of solvent left an amber, tacky resin, which was too viscous to form readily a homogeneous mixture with another equivalent of DDI.



Mole Ratio: 2:1

Plasticizer/Solvent: BDNPF/A, 22.2% on wt basis.

NWC TP 5995

Catalyst: Thermolite #12, 0.2%

Results: The initially fluid, homogeneous mixture was converted to a taffy-like product after two weeks at 25°C, when the isocyanate had almost completely disappeared.

Mole Ratio: 2:1

Plasticizer/Solvent: BDNPF/A, 45.3% on weight basis

Catalyst: Thermolite #12, 0.2%

Results: The system was always heterogeneous; the fluidity markedly decreased as the end-capped DDI was formed.

Mole Ratio: 2:1

Plasticizer/Solvent: IDP, 36.7% on weight basis

Catalyst: Thermolite #12, 0.3%

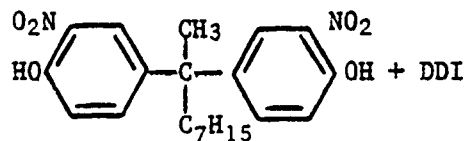
Results: A very fluid, homogeneous composition was rapidly attained when the ingredients were mixed. The mix was still fluid after 10 days at 25°C, at which time the end-capping reaction was complete. When another equivalent of DDI was added, the components mixed readily to yield a homogeneous solution. When fully cured, however, this uncrosslinked, highly plasticized binder was still molasses-like at 25°C.

Mole Ratio: 2:1

Plasticizer/Solvent: IDP, 27.6% on weight basis

Catalyst: Thermolite #12, 0.2%

Results: As in the previous experiment, a fluid, homogeneous mix was easily obtained. By heating at 55°C for 24 hr the end-capping reaction was essentially complete. The viscosity of this solution was 32.6 Pa·s at 25.1°C. When diluted with another equivalent of DDI and mixed until homogeneous (easily accomplished), the viscosity dropped to 8.7 Pa·s at 24.0°C. This last mix cured slowly at ambient temperature to a soft, tacky resin.



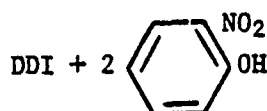
Mole Ratio: 2:1

Solvent: Dry THF (1.35 x weight of reactants).

Catalyst: Thermolite #12, approximately 0.5%

Results: When the end-capping reaction was complete (19 days), the solvent was removed; the resulting product was so very viscous that mixing at 25°C with another

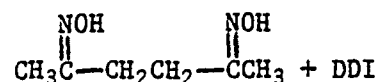
equivalent of DDI was not accomplished. Warming to 69-70°C with stirring was needed to get a homogeneous but now very fluid mix.



Dimer diisocyanate (3.0 g, 0.005 mole) and o-nitrophenol (1.39 g, 0.01 mole) were mixed, warmed slightly to dissolve the latter compound, re-cooled to 30°C, treated with four drops of pyridine and allowed to stand at ambient temperature. Although the o-nitrophenol recrystallized in part, it slowly redissolved as the reaction proceeded. More than 30 days were required for the isocyanate absorption to disappear from the infrared spectrum.

In a similar experiment in which 0.05 g of Thermolite #12 was used instead of pyridine, only about two weeks were required at ambient temperature to reach the same state of completion. This viscous end-capped, diisocyanate showed extensive dissociation when heated to 150°C for 5 min, then quenched to 30°C (increased NCO absorption, decreased urethane carbonyl at 1755 cm⁻¹ in the infrared spectrum). After 66 hr at ambient, the isocyanate absorption had almost completely disappeared again. This one cycle of heating, cooling and re-curing led, however, to a significant increase in the amount of uretidione present (carbonyl absorption about 1690 cm⁻¹).

MISCELLANEOUS SYSTEMS, INCLUDING BOTH POLYMERS AND MONOMERIC MODEL COMPOUNDS

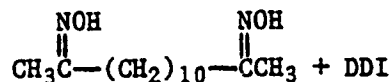


Mole Ratio: 1:1

Solvent: THF (2 parts by weight per part of reactants)

Catalyst: None

Results: This amount of solvent was needed to dissolve the dioxime. The reaction was mildly exothermic and was essentially complete after 5 hr at 25°C. Removal of the solvent after 22 hr left a tough, clear, colorless somewhat elastomeric resin. When heated to 150-155°C, it became very soft but also darkened; no evidence based on infrared spectrum of dissociation. Polymer after 21 months storage at 25°C was still soluble in THF.

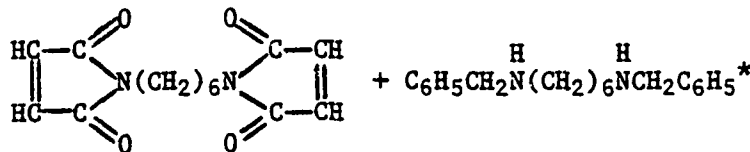


Mole Ratio: 1:1

Solvent: None

Catalyst: None

Results: When the 2,11-dodecanedione dioxime (m.p. 113-116°C) and the DDI were heated to 100°C, a clear, homogeneous melt was formed and polymerization occurred. At ambient, the product formed a tough clear film; at 145-148°C, it melted to a viscous liquid. The infrared spectrum indicated very little dissociation (no increase in NCO absorption).



Mole Ratio: 1:1

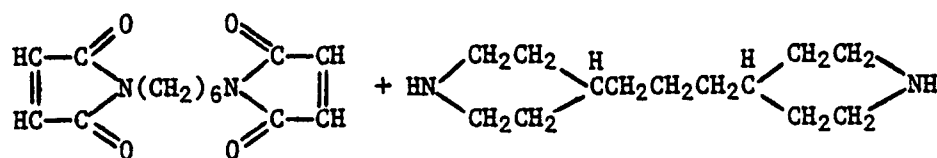
Solvent: THF (4 parts of solvent to 1 part of reactants)

Catalyst: None

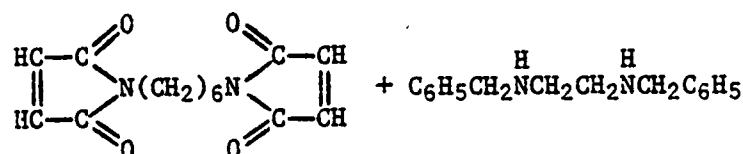
Results: Five days at ambient were required for complete solution of the bis-maleimide. After six days the infrared absorptions, due to both NH and to maleimide, had disappeared. Removal of the solvent left a tan, glassy resin; upon heating to 150°C for 5 min there was no indication of dissociation based on an infrared spectrum although the resin became very fluid. Without solvent there was very little condensation even after six days at 73°C.

* This liquid diamine was made by condensing 2 moles of benzaldehyde with 1 mole of 1,6-diaminohexane, followed by hydrogenation over PtO₂. ¹H NMR (CDCl₃, 60 MHz), δ 1.33 (broad s, 8H), 2.62 (t, 4H, -NH-CH₂-CH₂), 3.75 (s, 4H, C₆H₅CH₂), 7.30 (s, 10H, C₆H₅).

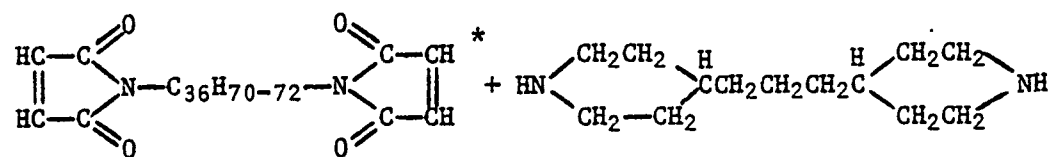
The dihydrochloride after recrystallization from ethanol melted 288-290°C. Anal. Calcd. for C₂₀H₃₀Cl₂N₂: Cl, 19.19; N, 7.59. Found: Cl, 19.17; N, 7.59. The dibenzoate (recrystallized from cyclohexane) melted 119°C. Anal. Calcd. for C₃₄H₄₀N₂O₄: C, 75.52; H, 7.46; N, 5.18. Found: C, 75.97; H, 7.60; N, 5.52.



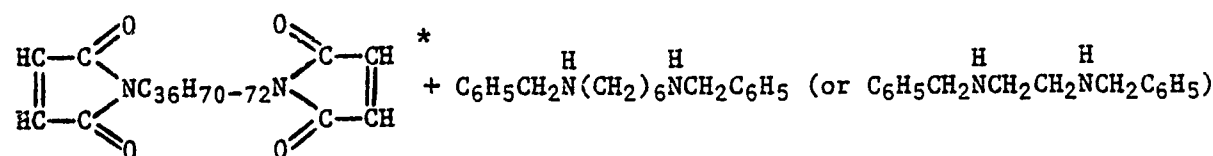
When equimolar amounts were held at 100°C and stirred, a polymer slowly formed (a homogeneous liquid was never attained). At 150°C this mass was soft, tacky and somewhat rubbery; it did not liquefy. The conclusion was that no appreciable dissociation to initial reactants occurred,



A tacky homogeneous gum was obtained by mixing equimolar quantities and heating at 100°C for 15 min.



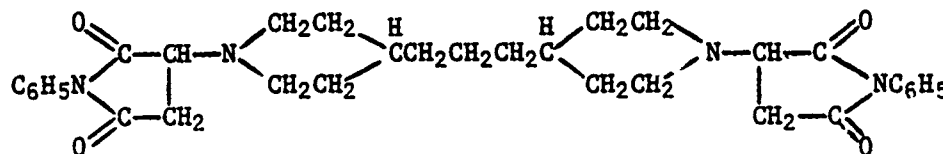
Equivalent quantities of co-reactants quickly yielded a homogeneous melt at 100°C. After 2 hr at 100°C the product was a pale amber, stiff gum. It did not melt at 150°C after 25 min; the soft, tacky product could be pulled into long rubbery strings.



Mole Ratio: 1:1
Solvent: None
Catalyst: None

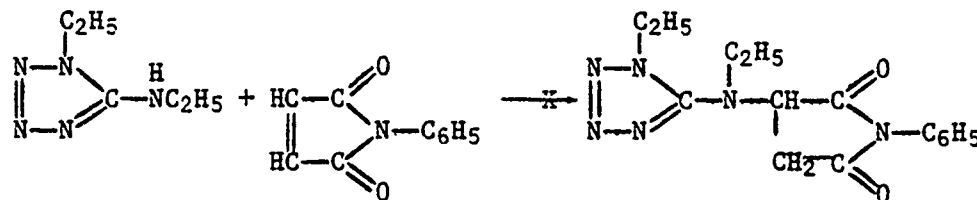
* See Appendix C for synthesis of this material.

Results: Upon mixing, the liquid reactants readily formed a homogeneous fluid. After 16 hr at 25°C the mix would no longer flow; 3 hr cure at 73°C gave a rubbery mass which was tacky, but not soft or liquid, when heated to 150°C. No indication of extensive thermal dissociation.

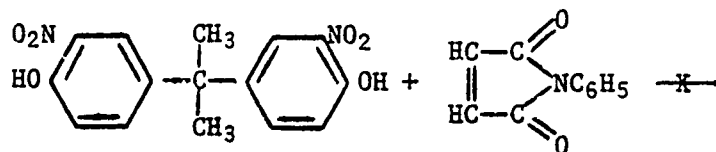


N-Phenylmaleimide and 1,3-di(4-piperidyl)propane (molar ratio of reactants 2:1) reacted exothermically at 60-70°C. Recrystallization from benzene-n-hexane (35:15) yielded a white powder which decomposed to a red liquid at 173-179°C. No evidence of a reversible dissociation.

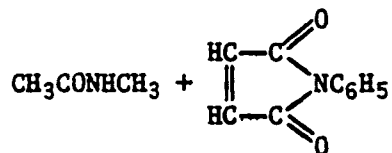
Anal. Calcd. for $C_{33}H_{40}N_4O_4$: C, 71.20; H, 7.24; N, 10.07. Found: C, 71.10; H, 7.45; N, 9.73.



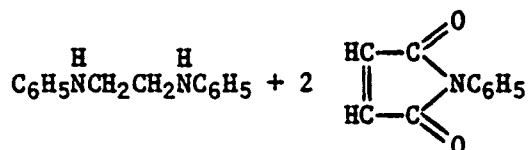
No reaction occurred after heating equivalent amounts of reactants at 100°C for 1-3/4 hr.



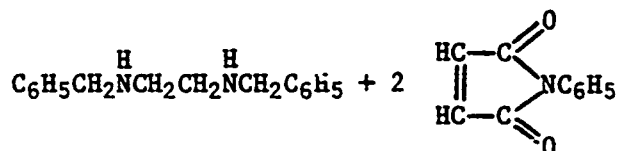
No reaction after 4.5 hr at 100°C.



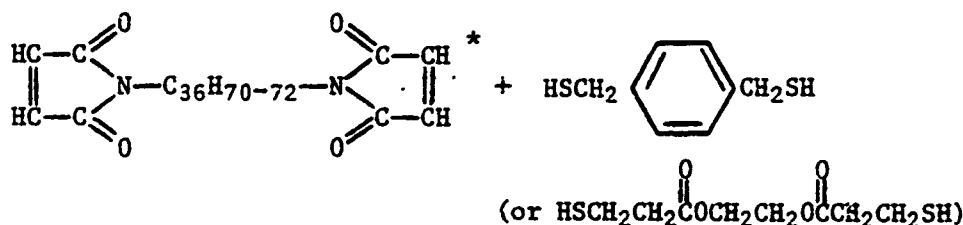
No reaction occurred when equimolar amounts were warmed enough to give a liquid, homogeneous melt.



No significant reaction was noted after heating the reactants at 100°C for 3 hr.



When mixed neat, an immediate exothermic reaction occurred (temperature rose ~ 15°C); a homogeneous melt was attained by raising the temperature to 90°C. Cooling gave an amber, viscous gum, soluble in benzene but not in cyclohexane.



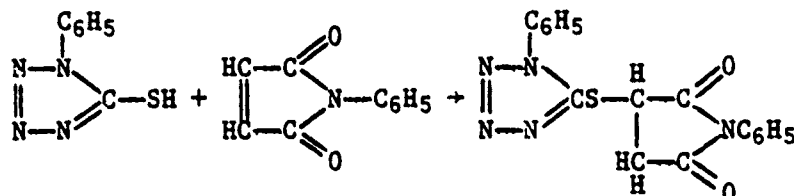
Mole Ratio: 1:1

Solvent: None

Catalyst: None

Results: The liquid, homogeneous mixtures had not polymerized after seven months at 25°C.

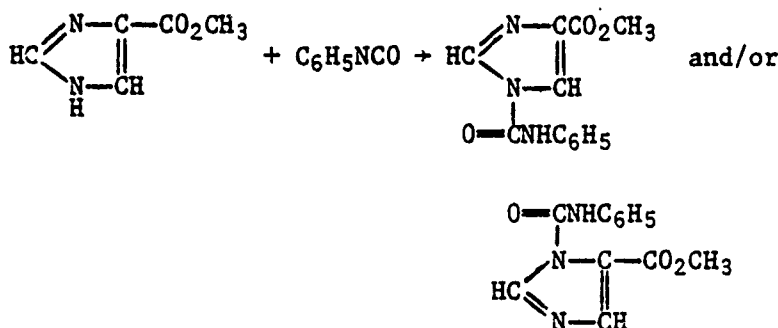
* See appendix C for synthesis of this material.



Equal weights of the two reactants were heated at 73°C for 63.5 hr. When the resulting amber glass was triturated with benzene, it soon crystallized. Recrystallization from benzene yielded off-white rosettes of felted needles; m.p. 163-164°.

Anal. Calcd. for $C_{17}H_{13}N_5O_2S$: N, 19.93; S, 9.12. Found: N, 19.92; S, 9.09.

When heated at 167°C for 4 min then quenched, there was no evidence for dissociation back to starting constituents.



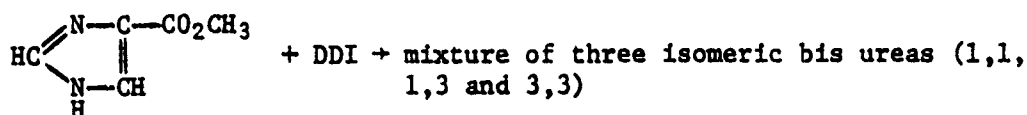
Methyl 4-imidazolecarboxylate* and phenyl isocyanate (equimolar amounts) were mixed without solvent and allowed to stand at room temperature until the odor of isocyanate disappeared. Recrystallization from dry benzene plus n-hexane gave white grains, m.p. 125-130°C, wet 110°C.

1H NMR (CDCl₃, 60 MHz), δ 3.83 (s, 3H, CCH₃), 7.0-7.8 (multiplet, C₆H₅), 8.32 (s, 1H, H₂ or H₅), 8.46 (s, 1H, H₅ or H₂). One sample showed two slightly different methyl signals and three different methine portions, suggesting a mixture of closely related isomers.

Anal. Calcd. for $C_{12}H_{11}N_3O_3$: N, 17.13. Found: N, 17.29.

When heated to 147°C for 4 min and quenched, isocyanate was evident both by odor and by the NCO absorption in the infrared spectrum.

* See Appendix C.



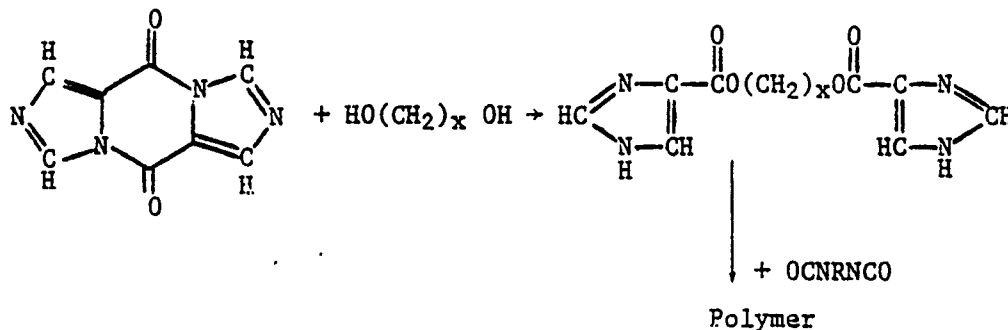
Mole Ratio: 2:1

Solvent: THF (2 parts per part of reactants)

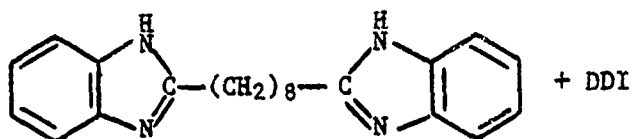
Catalyst: None

Results: The methyl ester was only partially soluble in the solvent; however, as the reaction proceeded more dissolved and the system was homogeneous after 24 hr at 25°C. After 48 hr all of the isocyanate had been consumed. Removal of the solvent left a sticky, very viscous end-capped DDI. When this mixture was heated to 150-155°C for 5 min, then quickly re-cooled to ambient temperature, an infrared spectrum revealed the re-appearance of a strong NCO absorption. After 24 hr the latter had again disappeared.

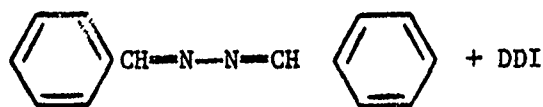
It had been the hope to make diesters of the following type by the reaction of diols with diimidazo[3,4-a:3',4'-d]piperazin-2,5-dione¹⁴ and to convert them to dissociable polymers by condensation with diisocyanates, but the yields of the diimidazo[3,4-a:3',4'-d]piperazin-2,5-dione were too low to make this an attractive route to another kind of polymer:



¹⁴ S. Kasina and J. Nematollahi. "A New and Simple Synthesis of Some 4-Substituted Imidazoles," *Synthesis*, Vol. 1975, p. 162.



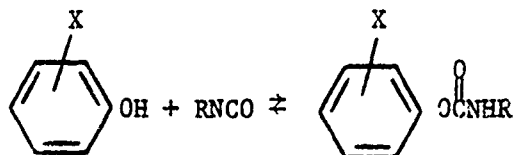
Solvent: Large excess of THF
 Catalyst: None
 Results: The bis-benzimidazole did not dissolve even in refluxing THF, hence little or no reaction with the diisocyanate.



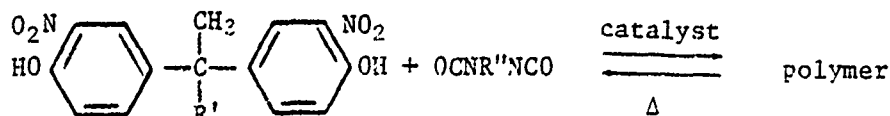
Mole Ratio: 1:1
 Solvent: None
 Catalyst: Thermolite #12
 Cure Temperature: Ambient and 70°C
 Results: A mixture consisting of equimolar amounts of the reactants was homogeneous at 70°C but heterogeneous at ambient. There was no indication of reaction at 20°C after several days; at 70°C, some homopolymerization of the DDI occurred.

DISCUSSION

Most of the investigation has been directed toward the utilization of the blocked isocyanate concept, and more specifically, the dinitro-bis-phenol-diisocyanate reaction. Initial efforts involved bis-phenol-A



(X is one or more electronegative groups, preferably in the ortho or para positions.)



I

since it is commercially available in ton quantities. Conversion to the 3,3'-dinitro derivative (I, $R' = CH_3$) is easily accomplished; however, this solid dinitro compound is only poorly soluble in the common diisocyanates and plasticizers used in binder formulations at ambient temperatures. Hence liquid prepolymer blends or mixes cannot be obtained directly. If the catalyzed condensation with a diisocyanate, such as DDI, is initially effected in a mutual solvent, such as tetrahydrofuran, the solvent can be removed after 24 hr to leave a very viscous, liquid resin which cures on further standing. This procedure introduces a troublesome extra step, especially since complete removal of the solvent from the viscous resin is difficult. In addition the resins, per se, are probably too viscous at this stage for satisfactory mixing of a PBX formulation although this deficiency could be overcome and controlled by incorporating a suitable plasticizer into the partially cured polymer prior to removal of the solvent.

Dinitro-bis-phenol-B (I, $R' = C_2H_5$) is also derived from another commercially available material. Although it has a lower melting point and is generally somewhat more soluble* than dinitro-bis-phenol-A, especially at 50-70°C, in the diisocyanates and plasticizers, it suffers from most of the same disadvantages. A mutual solvent, although less in quantity, would be required in the early stages of the condensation.

The difficulties introduced by the poor solubility of dinitro-bis-phenol-A or -B were overcome by increasing the length of the R' group in I to six or seven carbons. Both 2,2-bis(3-nitro-4-hydroxyphenyl)octane and nonane were low melting solids (easily stored as supercool liquids) which readily formed fluid homogeneous solutions with diisocyanates, such as DDI, without necessitating the use of a mutual solvent or extraneous plasticizer. The disadvantage in using these compounds is the fact that the starting 2,2-bis(4-hydroxyphenyl)alkanes are not offered commercially; they are made, however, in high yields from readily available chemicals as described in Appendix B.

As with the preparation of other polyurethanes, the rate of condensation of the diisocyanate with the dinitro bis-phenol can be accelerated by the presence of a catalyst. Without catalyst, mixtures of DDI and 2,2-bis(3-nitro-4-hydroxyphenyl)octane or nonane have stood at ambient temperature for more than six weeks with very little condensation, based on the appearance and growth of the urethane carbonyl absorption in the infrared spectrum. Tertiary amines such as pyridine, pyridine derivatives, DABCO, etc., effected a slow condensation at ambient. Ferric acetylacetonate for this type of system proved to be a very poor catalyst; even at 55-60°C after many days little or no condensation occurred. Thermolite #12 which

* For example, an equimolar mixture of DDI and dinitro-bis-phenol-B, plasticized with 20 weight percent of isodecyl pelargonate, was a fluid, homogeneous mix at 60°C.

is readily soluble in these systems, was the best catalyst examined.* At the 0.1-0.2% level after 24-48 hr at 55-60°C or one to two weeks at ambient, a high level of cure was effected (significant decrease or complete disappearance of the isocyanate absorption in the infrared spectrum, together with a correspondingly large increase in the urethane carbonyl absorption). Triphenyl bismuth appeared to be a less efficient catalyst than Thermolite #12 although this could be related to what seems to be a poorer solubility in the binder mix; the point was not examined closely.

The polyurethane derived from DDI and dinitro-bis-phenol-A was a tough, clear, orange-red resin. As would be expected, the product from DDI became somewhat softer and tackier as the R' group in I was increased to six or seven carbon atoms, but even then cuts on the surface of the resin would remain unhealed after several weeks at ambient temperature. Plasticizing the resin from DDI and 2,2-bis(3-nitro-4-hydroxyphenyl)-octane with 20-21% IDP furnished a soft material which would cold flow at ambient temperature. Similar results were obtained with DDI and dinitro-bis-phenol-B. (For some reason, complete cure, as measured by the disappearance of the isocyanate absorption in the infrared spectrum, was never attained in either of these systems.) Crosslinking with 9 mole percent of Desmodur N-100 increased the elasticity of the polymer from 2,2-bis(3-nitro-4-hydroxyphenyl)propane; this aspect of controlling the rubbery nature of the dissociable binder by the extent of crosslinking was not carefully examined. When the DDI was replaced by 1,6-hexamethylene diisocyanate in the polyurethane from 2,3-bis(3-nitro-4-hydroxyphenyl)-octane, the resin was hard and brittle.

These polyurethane resins appear to have good adhesive properties, bonding well to glass, powdered sodium sulfate, sodium chloride, etc. For example, films pressed between sodium chloride windows would occasionally pull out pieces of the sodium chloride when the windows were separated.

Proof that the urethane bonds would reversibly dissociate in these resins was obtained by heating cured polymer to 145-150°C until liquid. When quenched to ambient temperature, the resin remained as a viscous liquid; after several days at ambient it would re-cure to the same tough

* When 0.01 molar quantities of phenyl isocyanate and o-nitrophenol were warmed to 40-45°C, swirled to give a homogeneous melt, treated with 0.05 g of Thermolite #12, and allowed to cool to ambient, crystals of product began to separate within one hour. After 3 hr the solid white mass was essentially free of isocyanate. By way of comparison, when two drops of pyridine were employed as the catalyst instead of the tin salt, about 24 hr were required to give a solid, isocyanate-free product.

resin. Changes in the infrared spectrum (see Figure 1) confirm that urethane links dissociate during the heating-quenching cycle (increased isocyanate absorption, decreased urethane carbonyl), and re-form when the polymer re-cures (disappearance of isocyanate and increased urethane carbonyl absorption). The presence of plasticizer did not interfere with the dissociation/re-cure when samples were cycled to 146°C, quenched to 25°C and allowed to stand at ambient temperature for several days. The polymers derived from DDI can be held at 145-150°C for at least two hours provided the heating is done under dry nitrogen; if done under air, gellation occurs after about 30 min, probably as a consequence of oxidation. With longer heating or more cycles of dissociation/re-cure, the amount of uretidione, resulting from homopolymerization of the isocyanate groups, seems to increase slowly. Some loss or alteration in polymer properties would result.

To ascertain whether dissociation, liquefaction and re-cure would occur in a filled composition, simulating a PBX, the following experiment was performed: polymer derived from DDI and dinitro-bis-phenol-A in THF was used to coat oven-dried, powdered sodium sulfate (20% binder, 80% filler). After removal of the solvent at 73°C, 25 mm, the resulting molding powder was pressed into pellets at 40,000 psi. A pellet heated at 100°C for 2 hr became soft, but there was only slight slumping. After 6 min at 153-155°C, a pellet slumped and flowed slowly; the composition was quite soft and easy to stir. Upon re-cooling to 25°C and standing for 24 hr, the mass again became solid and tough.

Numerous attempts were made to prepare prepolymers by end-capping DDI with molecules which would furnish the requisite bis-ortho-nitrophenol structure. Such prepolymers should then be converted into a dissociable polymer by chain-extension or crosslinking with additional di- or tri-isocyanate. There are several reasons for interest in such end-capped prepolymers. It is a way to increase the equivalent weight of the prepolymers into a more desirable range than the present 150-250 for the dinitro-bis-phenols, and 300 for the DDI. With higher molecular weight prepolymers, there will be less shrinking during final cure. Hopefully, the poorly soluble but more accessible dinitro-bis-phenol-A and -B (or related materials) could be converted into prepolymers which would be readily soluble in and easily mixed with the additional diisocyanate needed for chain-extension and cure. Proper end-capping should also permit alteration and/or control of the viscosity of the prepolymers.

Two types of end-capped prepolymers which were investigated are depicted as "a" and "b" in Figure 2. (R" is the 36 carbon atom moiety present in DDI, but it could be the radical present in other diisocyanates). The hoped-for advantages for end-capping were only partially realized with these examples. In general, the end-capping process had to be done in a mutual solvent, such as THF, which then had to be removed (frequently with difficulty) from the prepolymer; also a urethane catalyst had to be employed to effect the condensation. (It had been hoped that the primary

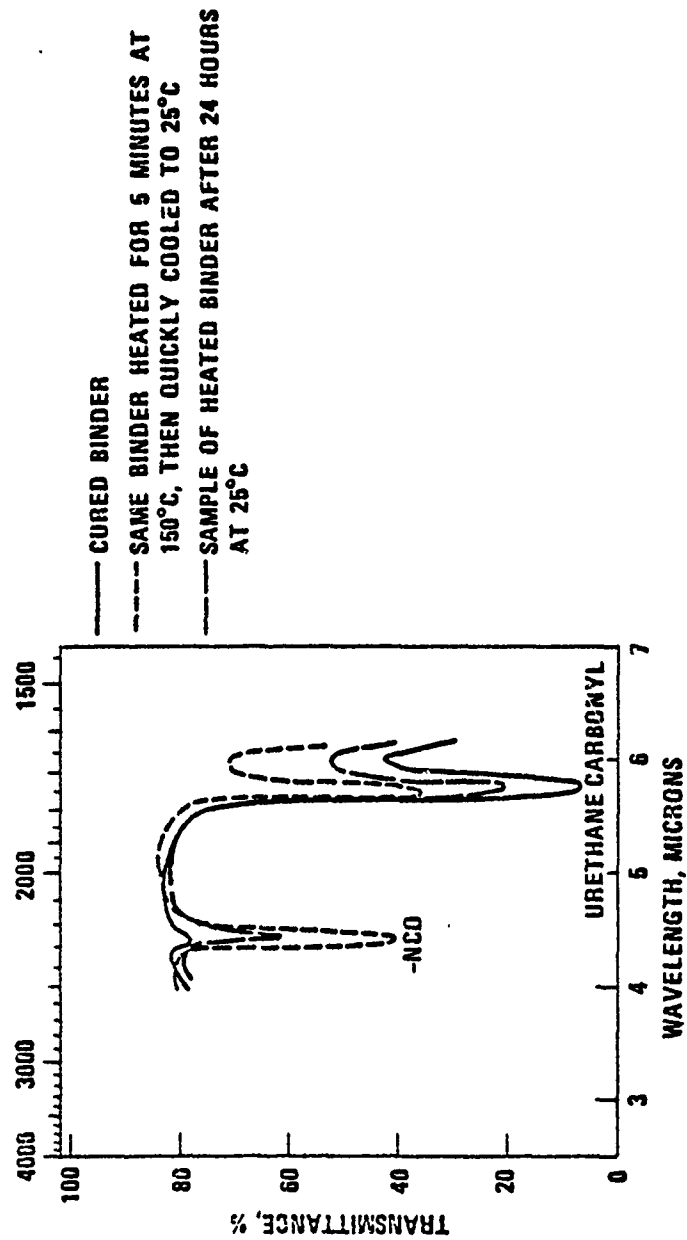


FIGURE 1. Spectral Changes During Dissociation and Re-cure of Polyurethane Binder.

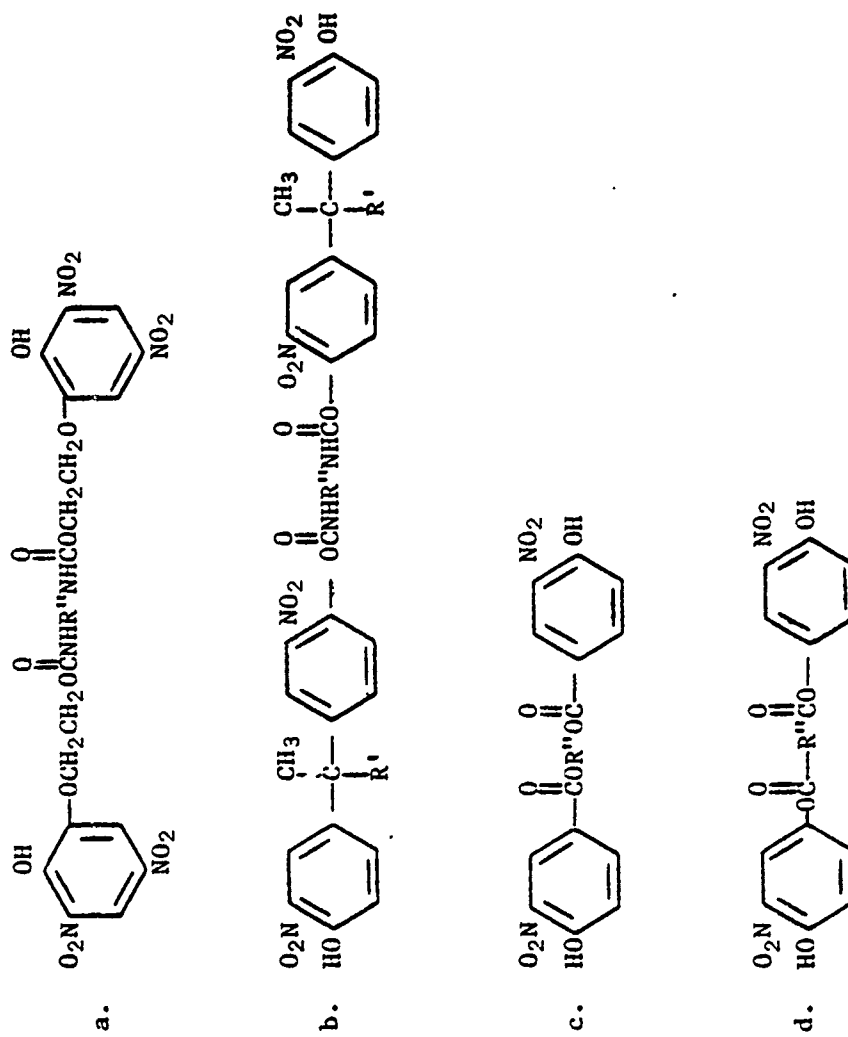


FIGURE 2. Other Dinitro-bis-phenols.

aliphatic hydroxyl group in the dinitro hydroxyethyl catechol used in example "a" could be reacted conveniently with isocyanate in the absence of catalyst.) The products from this end-capping stage were either brittle solids or exceedingly viscous liquids; in either case, mixing with more diisocyanate was very difficult and slow, even upon warming, and because of the presence of the urethane catalyst left from the initial condensation, much homopolymerization of the isocyanate occurred before homogeneous mixtures were obtained. By effecting the end-capping in a plasticizer, it was possible to obtain solutions of the prepolymers which had an adequate viscosity and which readily mixed with more diisocyanate for chain-extension (see earlier Experimental Section for details).

Two other bis-ortho-nitrophenol derivatives containing ester groups were made ["c" in Figure 2 with $R'' = (CH_2)_6$ or $(CH_2)_{10}$]; the intent again was to get compounds which either would be easily soluble in various diisocyanates without requiring a mutual solvent or plasticizer or would have higher equivalent weights than the best dinitro-bis-phenols. Although the synthesis of the diesters from diols and p-hydroxybenzoic acid was straightforward, the conversion to the dinitro compound demanded much more vigorous nitration conditions than were needed with the bis-phenols, illustrating the dramatic deactivating effect of the carbonyl group on the aromatic ring toward electrophilic attack. Unfortunately, these dinitro esters were insoluble or poorly soluble in DDI and only sparingly soluble in THF (or even boiling ethanol). Because of this poor solubility, attempts at polyurethane formation were not very successful or promising.

Diesters of the type "d", Figure 2, were considered but were not made because of the poor results obtained with the previous kinds of diesters. Several other kinds of bis-(ortho-nitrophenol) derivatives were synthesized and are described in the Experimental Section; none of these compounds was satisfactory for one reason or another.

Two other polyurethanes were investigated (see equations "a" and "b" in Figure 3). The crystalline, fluorinated diol in "a"¹⁵ was made photochemically from ethane and hexafluoroacetone; it reacted catalytically with DDI (see Experimental) to yield a clear, almost colorless, polymer which dissociated reversibly with liquefaction when heated to 145-150°C and re-cured when cooled to ambient temperature and allowed to stand. Like the results with the polyurethanes from the dinitro-bis-phenols, changes in the infrared spectra also reflected the reversible nature of the dissociation/re-cure. Probably because of the nature of the catalyst used, there appeared to be an increasing amount of uretidione formed when this cycling operation was repeated several times.

¹⁵ J. H. Johnson, A. S. Gordon, and W. P. Norris. Fluorinated Compounds. 15 February 1977. U. S. Patent 4,008,139; A. S. Gordon, W. P. Norris, R. H. Knipe, and J. H. Johnson. "Photochemically Induced Reaction Between Perfluoroacetone and Ethane," *Int. J. Chem. Kinet.*, Vol. VII (1975), pp. 15-22.

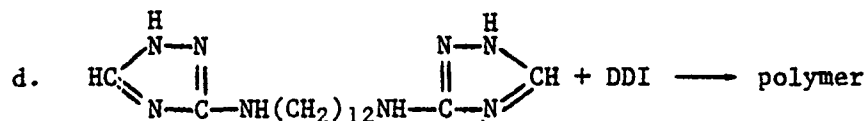
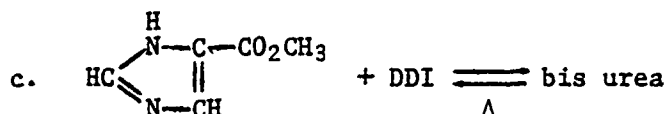
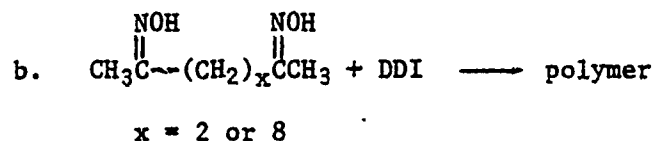
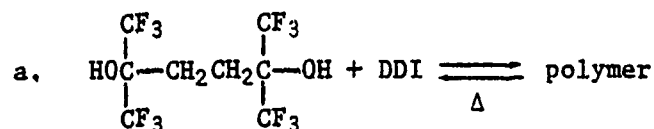
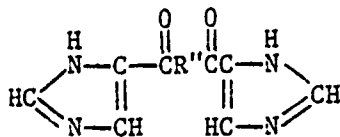


FIGURE 3. Other Types of Polyurethanes and Polyureas

The reaction of DDI with the bis-oximes proceeded readily without catalyst to furnish polymers ("b" in Figure 3); although these polymers became quite soft, they did not dissociate at 140-150°C, based on the infrared spectrum.

As reported earlier,⁷ weakly basic amines react with isocyanates to give ureas which will dissociate at elevated temperatures. This was again demonstrated both with the bis-urea from DDI and two moles of methyl 4-imidazolecarboxylate ("c" in Figure 3) and with the urea from phenylisocyanate and the same ester. The intent was then to prepare diesters end-capped with imidazole groups and to condense these with diisocyanates to make reversibly dissociable polymers; but as discussed in the Experimental Section, these efforts were frustrated by a failure to obtain adequate precursors to the desired diesters. Other efforts to prepare bis-2- or 4-acylimidazoles, similar to the following, were also unsuccessful.



The bis-(amino-1,2,4-triazoyl)alkane, shown in "d", Figure 3, and mixed with isomeric compounds, was made by a two step synthesis. Although this very poorly soluble mixture of isomeric compounds condensed slowly with DDI, the resulting rubbery polyurea showed no signs of significant dissociation when heated to 140-150°C. A common difficulty to be expected with α,ω -disubstituted alkanes, where the substituents are heterocyclic groups, is their high melting point and low solubility; consequently, they do not lend themselves to easy and convenient utilization in castable binder formulations. Other examples illustrating this point can be found in the Experimental Section.

Several polymers derived from bis-maleimides were prepared since reports in the literature (see Introduction) suggested that some of these might dissociate reversibly. Two general classes are depicted on Figure 4; the various experiments performed are detailed in the Experimental Section, pages 20-22. Although tough, rubbery polymers were very readily formed from bis-maleimides and bis-secondary amines, dissociation of the polymers did not seem to occur in the range of 140-150°C. The polymers would become soft but did not liquefy. This system is also impractical from a formulation standpoint since the rate of polymerization, when the comonomers are mixed, is much too fast (exothermic in some cases) and the pot life before gelation much too short.

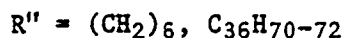
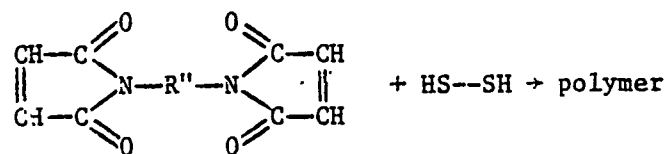
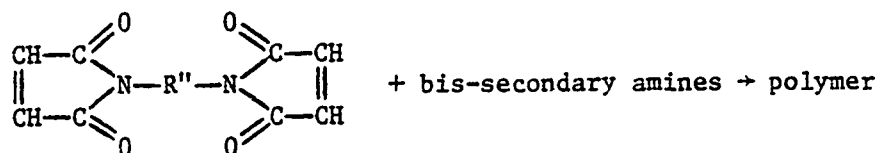


FIGURE 4. Polymers From Bis-Maleimides.

On the other hand, the results with bis-thiols as chain-extenders for bis-maleimides were mixed. Some thiols did not react, others reacted slowly upon heating, and some reacted at a moderate and practical rate at ambient temperature. For example, the bis-maleimide from dimer diamine (General Mills) and mercaptan terminated butadiene-acrylonitrile copolymer (HYCAR MTEN) polymerized after ten days at 25°C to a clear, tough binder; no extraneous catalyst was needed. This material, however, again did not dissociate when heated to 160°C for 45 minutes.

Only a very limited effort was directed toward the development of polymers based on dissociable bonds derived from or utilizing the C-nitroso group (either nitroso dimers or suitable nitroso-diene adducts). The main reason for this limited effort was the difficulty encountered in synthesizing the bis-nitroso compounds. In addition, those that were made proved to be solid and poorly soluble in the liquid co-reactants needed to make polymer. With greater effort, low melting or liquid, soluble bis-nitroso compounds probably could have been designed and synthesized, just as was ultimately accomplished with the dinitro-bis-phenols. The experimental results obtained under this program with the nitroso compounds are summarized in Appendix D.

CONCLUSIONS

The feasibility of a reversibly dissociable polymeric binder has been demonstrated with the polyurethane system from a diisocyanate and 2,2-bis-(3-nitro-4-hydroxyphenyl)alkane. The most suitable co-reactants examined to date are either commercially available or readily prepared from commercially available compounds. The most promising system is a homogeneous liquid with excellent pot life; cure conditions are reasonable (one to three weeks at ambient temperature, two to three days at 55-60°C, Thermolite #12 as catalyst). Liquefaction with dissociation of urethane bonds at 140-150°C occurs readily; upon standing at ambient temperature, urethane linkages slowly re-form and the material again becomes a tough resin.

Appendix A

SYNTHESES OF POTENTIAL DESENSITIZING WAXES

Quantities of 2-nitro-4-t-butylphenol and 2-nitro-4-octylphenol were made and purified by chromatography on silica gel (see following sections). The interest in these materials stems from the possibility of preparing from them synthetic, desensitizing waxes of the type



which will be able to absorb energy at a hot spot not only through the latent heat of fusion at the melting point, but through the endothermic dissociation of the urethane linkage at a somewhat higher temperature. This second heat sink should provide an additional factor of safety. As with the reversible, dissociable polymers, the desensitizer should reform when the hot spot is cooled. Several urethanes of this type were prepared and are described below. None is probably suitable for the purpose intended since the waxy character appears to be insufficient and/or the melting points are either too high or too low when compared with that of Grade A desensitizing wax (m.p. 78.3-87.8°C).

2-NITRO-4-t-BUTYLPHENOL

With cooling, so as to keep the temperature 25-30°C, and vigorous stirring, 167 ml of 3N nitric acid (0.5 mole) was added over 40 min to a solution of 37.5 g (0.25 mole) of 4-t-butylphenol in 150 ml of benzene. After 25 ml of acid had been introduced, 0.2 g of sodium nitrite was added. Stirring at 24-25°C was continued for 1 hr more. The color of the solution changed from dark-olive to red-orange. The aqueous acid layer was separated and the benzene layer washed twice with 50 ml portions of cold water. Evaporation of the benzene left 46.7 g (96%) of liquid nitrophenol which contained only 3-4% of dinitro derivative based on the ^1H NMR spectrum. The crude product was chromatographed on silica gel using 1:1 cyclohexane-benzene as the solvent; the recovery was about 96% (a small forerun was mainly 6-nitro-2,4-di-t-butylphenol). ^1H NMR

(CDCl₃, 60 MHz), δ 1.34 (s, t-butyl), 7.15 (d, 1H, H₂, J_{H₂H₃} = 8.5 Hz), 7.77 (dd, 1H, H₃, J_{H₂H₃} = 8.5 Hz, J_{H₃H₅} = ~2 Hz), 8.15 (d, 1H, H₅, J_{H₃H₅} = ~2 Hz).

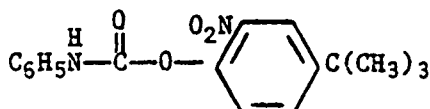
When the nitration was done with 0.72 mole of 3N nitric acid, the amount of dinitro phenol in the crude product was increased to about 7%; with 0.72 mole of 4N nitric, the content of dinitro was 10-15%; and with 0.72 mole of 6N, still greater. From the latter experiment it was possible to isolate some of the 2,6-dinitro-4-t-butylphenol by dissolving the crude product in hexane and cooling to -15°C. After recrystallization from methanol, the compound melted 93-94°C. ¹H NMR (CDCl₃, 60 MHz), δ 1.38 (s, 9H, t-butyl), 8.56 (s, 2H, H₃, H₅), 11.45 (s, H, OH).

2-NITRO-4-OCTYLPHENOL (the C₈H₁₇ group is a branched chain alkyl group)

Commercial 4-octylphenol (51.5 g, 0.25 mole) was dissolved in 150 ml of benzene; with vigorous stirring and cooling to keep the temperature 25-30°C, 170 ml of 3N nitric acid (0.5 mole) was added during 40 min. After 20 ml of acid had been added, 0.3 g of sodium nitrite was introduced into the reaction flask; an exotherm began and the solution became very dark colored. Stirring was continued for 1 hr and 20 min at 24-26°C after the acid had all been added. The benzene layer was separated, washed with three 50 ml portions of water, and evaporated to leave 61.9 g (97%) of a very dark, viscous liquid product. It was chromatographed over silica gel using 1:1 cyclohexane-benzene as the eluent. The forerun, 2.4 g, had an ¹H NMR spectrum which suggested mainly mono-nitro-di-octylphenol. The main fraction, 48.0 g, was pale red-orange in color. The ¹H NMR spectrum agreed with that expected for the desired mono-nitro compound.

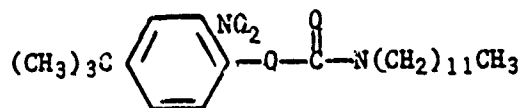
Anal. Calcd. for C₁₄H₂₁NO₃: N, 5.57. Found: N, 5.76.

When the nitration was done with 0.72 mole of 6N nitric acid under otherwise similar conditions, both the nitrogen analysis (6.66, 6.69%) and the ¹H NMR spectrum indicated that the crude product contained about 35% dinitro- and 65% mono-nitro derivatives.



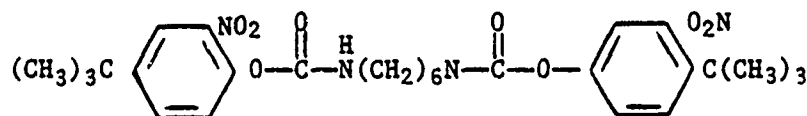
This urethane melted 119-120°C after recrystallization from cyclohexane plus benzene.

Anal. Calcd. for C₁₇H₁₈N₂O₄: N, 8.91. Found: N, 8.78.

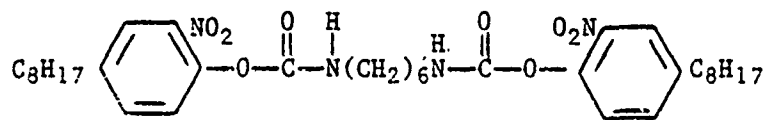


A solution of 15.0 g of chromatographed 2-nitro-4-*t*-butylphenol, 15.6 g of *n*-dodecyl isocyanate, 0.11 g of Thermolite #12 and 25 ml of dry benzene was allowed to stand for 40 days at room temperature, re-fluxed for 3 hr, cooled, diluted with 50 ml of *n*-hexane, and chilled to -15°C . The solid was filtered off in a cold funnel, washed once with 10 ml of cold 2:1 hexane-benzene, and vacuum dried; 9.6 g, m.p. $43-45^{\circ}\text{C}$. One recrystallization from 50 ml of *n*-hexane (cooling to -15°C required) gave a white powder, m.p. $44-46^{\circ}\text{C}$.

Anal. Calcd. for $\text{C}_{23}\text{H}_{38}\text{N}_2\text{O}_4$: N, 6.89. Found: N, 6.78.

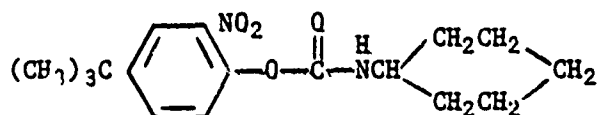


Four months at ambient temperature were required for 15.9 g of 2-nitro-4-*t*-butylphenol and 6.8 g of hexamethylene diisocyanate to react in 20 ml of dry benzene, using 0.13 g of Thermolite #12 as catalyst. After recrystallization from benzene the bis-urethane melted $138-140^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 60 MHz), δ 1.34 (s, *t*-butyl), 1.46 (part of $-\text{CH}_2-$ multiplet), 3.30 (d, 4H, $-\text{NH}-\text{CH}_2$), 5.50 (t, 2H, $-\text{NH}-\text{CH}_2-$), 7.27 (d, 2H, H_6 , $J_{\text{H}_5\text{H}_6} = 8.5$ Hz), 7.72 (dd, 2H, H_5 , $J_{\text{H}_5\text{H}_6} = 8.5$ Hz, $J_{\text{H}_3\text{H}_5} = \sim 2$ Hz), 8.08 (d, 2H, H_3 , $J_{\text{H}_3\text{H}_5} = \sim 2$ Hz).



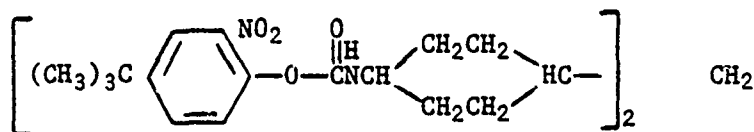
This bis-urethane was made as in the previous experiment except that two equivalents of 2-nitro-4-octylphenol were condensed with one equivalent of hexamethylene diisocyanate. After recrystallization from cyclohexane (6.2 g/80 ml) the compound melted $66-67^{\circ}\text{C}$; after drying at 55°C , 25 min, for five days the melting point was $88.5-89.5^{\circ}\text{C}$.

Anal. Calcd. for $\text{C}_{36}\text{H}_{54}\text{N}_4\text{O}_8$: N, 8.35. Found: N, 8.65.



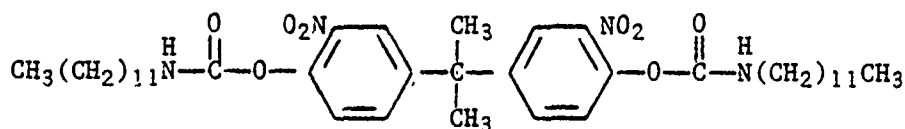
The procedure was similar to that used in the previous experiments except that equimolar amounts of 2-nitro-4-*t*-butylphenol and cyclohexyl isocyanate were reacted in dry benzene. Since the condensation was still not complete after three months at ambient, the solution was re-fluxed for 7 hr, cooled to 25°C, diluted with two volumes of *n*-hexane, and allowed to stand; white, felted clumps, m.p. 103-105°C, separated. Adding more hexane and cooling to 5°C furnished more product; the total yield was 5.7 g (35% of theory). After recrystallization from cyclohexane, followed by vacuum drying at 70°C, 25 min, the m.p. was 103-104°C.

Anal. Calcd. for $C_{17}H_{24}N_2O_4$: N, 8.75. Found: N, 8.81.



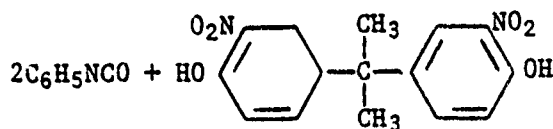
From Hylene-W (0.01 mole) and 2-nitro-4-*t*-butylphenol, catalyzed with Thermolite #12. The product was a brittle, pale yellow resin. Although the 1H NMR was in agreement with the structure, the infrared spectrum revealed the presence of some isocyanate.

Anal. Calcd. for $C_{35}H_{46}N_4O_8$: N, 8.61. Found: N, 8.80.



Recrystallized 2,2-bis(3-nitro-4-hydroxyphenyl)propane (3.7 g, 0.0116 mole) and 5.0 g (0.0237 mole) of *n*-dodecyl isocyanate were dissolved in 30 ml of dry tetrahydrofuran; 0.05 g of Thermolite #12 was added and the solution allowed to stand for one month. A trace of insoluble material was removed by filtration and the filtrate evaporated to dryness; recrystallization of the pale yellow solid from dry benzene furnished 6.2 g (72%) of product, m.p. 121-124°C.

Anal. Calcd. for $C_{41}H_{54}N_4O_8$: N, 7.56. Found: N, 7.67.



Mole Ratio: 2:1

Solvent: THF (1.6 parts per part of reactants)

Catalyst: Thermolite #12 (1.7%)

Results: After five days at ambient the reaction was complete, the THF was evaporated under reduced pressure to leave a pale yellow glass. Trituration with dry benzene gave 2.1 g of solid melting 125-130°C with bubbling followed by resolidification and remelting at 140-150°C. Another recrystallization gave a product which behaved the same except that the second melting was 154-158°C. The change at 125-130°C is probably a desolvation since the elemental analyses indicate the presence of benzene. Calcd. for $\text{C}_{29}\text{H}_{24}\text{N}_4\text{O}_8 \cdot 1.5\text{C}_6\text{H}_6$: N, 8.32. Found; N, 8.34.

UNSUCCESSFUL ATTEMPTS TO MAKE SYNTHETIC WAXES

Essentially no reaction occurred when 2-nitro-4-t-butylphenol (2 mole) and isophorone diisocyanate (1 mole) were heated at 70°C for 14-1/2 hr with Thermolite #12 present as catalyst.

Appendix B

SYNTHESIS AND PROPERTIES OF DIFUNCTIONAL
ORTHO-NITRO-PHENOLIC PRECURSORS

PREPARATION OF 2,2-BIS(4-HYDROXYPHENYL)ALKANES

The general procedure of Reid and Wilson¹⁶ was followed. The progress of the condensation was monitored with nuclear magnetic resonance (NMR). The preparation of 2,2-bis(4-hydroxyphenyl)octane is typical.

A 1 liter two-necked, round-bottomed flask fitted with a fritted glass gas delivery tube and a magnetic stirring bar was charged with 141.2 g (1.5 mole) of phenol and 64.1 g (0.5 mole) of 2-octanone. The resulting solution was stirred at room temperature while a slow stream of hydrogen chloride was bubbled in over a period of 6-1/2 hr; 7.7 g was absorbed. After standing overnight the mixture absorbed an additional 1.0 g over about 7-1/2 hr.

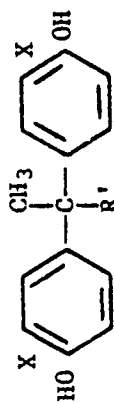
Crystallization of the mixture occurred between 48 and 72 hr reaction time and the reaction was complete after 168 hr (NMR). One hundred ml of hot water was added and the mixture was subjected to steam distillation until a FeCl_3 test for phenol was negative; about 2.2 liters of distillate were collected.

The water layer was decanted, the viscous, brown residue dissolved in 700 ml of warm (70°C) 1,2-dichloroethane, and the solution gravity filtered through a warm (60°C) jacketed funnel. Crystallization of the product was allowed to proceed at 5°C. Yield: 123.5 g (82.8%) of light tan solid; m.p. 88-91°C (uncorr.).

Melting points for several bis-phenols are listed in Table B-1.

¹⁶ E. Emmec Reid and Edith Wilson. "The Relation of Estrogenic Activity to Structure in Some 4,4'-Dihydroxydiphenylmethanes," *J. Am. Chem. Soc.*, Vol. 66 (1944), pp. 967-69.

TABLE B-1. Properties of Bis-phenols and Dinitro-bis-phenols.



R'	X=H m.p., °C	X=NO ₂ m.p., °C	Theory	Analysis % nitrogen		
				Recryst.	Chromato- graphed ^a	Crude ^b
CH ₃	153-156	132-135 ^c	8.81	8.44, 8.53	...	...
C ₂ H ₅	125-128	77-80 ^d	8.43	8.69	...	8.35
n-C ₄ H ₉	123.5-124.5 ^e	78-79	7.77	7.64	7.68	...
n-C ₅ H ₁₁	66.5-70	76-78	7.48	7.41	7.48	...
n-C ₆ H ₁₃	88-91	54-56	7.21	...	7.17	7.19 ^f
n-C ₇ H ₁₅	42-46.5	57-60	6.96	6.99	6.83	6.84

^a Material recovered by chromatography on silica gel.^b Material recovered from nitration reaction and before chromatography.^c ¹H NMR (CDCl₃, 60 MHz, δ 1.68 (s, 6H, CH₃), 7.08 (d, 2H, H₅, H_{5'}, J_{H₅H₆} = 8.5 Hz), 7.36 (dd, 2H, H₆, H_{6'}, J_{H₅H₆} = 8.5 Hz, J_{H₂H₆} = ~2 Hz), 8.07 (d, H₂, H_{2'}, J_{H₂H₆} = ~2 Hz).^d ¹H NMR (CDCl₃, 60 MHz), δ 0.78 (t, 3H, CH₂CH₃), 1.67 (s, 3H, -CCH₃), 2.18 (q, 2H, -CH₂CH₃), 7.15 (d, 2H, H₅, H_{5'}, J_{H₅H₆} = 8.5 Hz), 7.43 (dd, 2H, H₆, H_{6'}, J_{H₅H₆} = 8.5 Hz, J_{H₂H₆} = ~2 Hz), 8.13 (d, 2H, H₂, H_{2'}, J_{H₂H₆} = ~2 Hz), 10.7 (s, 2H, OH).^e Anal. Calcd. for C₁₈H₂₂O₂: C, 79.96; H, 8.20. Found: C, 79.31; H, 8.06.^f Crude product in benzene was stirred with decolorizing carbon for 16 hr, filtered and evaporated.

NITRATION OF 2,2-BIS(4-HYDROXYPHENYL)ALKANES

The following preparation of 2,2-bis(3-nitro-4-hydroxyphenyl)octane is typical. With vigorous stirring and cooling to keep the temperature in the range 25-30°C, 340 ml of 3N nitric acid was added dropwise during 40 minutes to a solution/slurry of 74.6 g (0.25 mole) of 2,2-bis(4-hydroxyphenyl)octane in 300 ml of benzene. After the first 50 ml of nitric acid had been introduced, 0.4 g of sodium nitrite was added; a mild exotherm ensued and the reaction mixture became dark orange-red. All of the starting bis-phenol had dissolved by the time the acid addition was completed; the color of the solution gradually lightened. The mixture was stirred for 2 hr more at 25-27°C. The benzene layer was then separated, washed thoroughly with three 200 ml portions of water, and evaporated under reduced pressure until the viscous, liquid product was free of volatiles. The yield was 94.3 g (97.5% of theory for a dinitroderivative). A thin layer chromatogram (tlc) indicated that this crude material was 85-90% of the dinitro derivative, with the balance about equal parts of the mono and trinitro derivatives. An 88% recovery of dinitro compound, based on the weight of crude product, could be effected by chromatographing the latter on silica gel using benzene as the eluent.

Anal. Calcd. for $C_{20}H_{24}N_2O_6$: N, 7.21. Found: N, 7.17, 7.13, 7.08.

Although the chromatographed product was obtained as a very viscous liquid, which would remain in this state for weeks if not seeded, the compound could be induced to crystallize by dissolving 2.5 g in 15 ml of absolute ethanol and chilling at 5°C for several days; m.p. 54-56°C.

Properties of other dinitro-bis-phenols are summarized in Table B-1. The yields of the crude dinitro compounds obtained from the C-4, C-6, C-7 and C-9 alkanes were comparable to that for the C-8, namely 97-100% of theory. The recovery on chromatography also was in the range 86 to 89%.

SOLUBILITY STUDIES ON DINITRO-BIS-PHENOL-A

One-half gram of dinitro-bis-phenol-A partially dissolved in 0.5 g of polycaprolactone (PCP 0300, Union Carbide) when heated to 70°C and stirred for 5 hr. Recrystallization occurred upon re-cooling to ambient temperature.

Dinitro-bis-phenol-A (1.65 g) did not dissolve in 4.65 g of BDNPF/A after stirring at 25°C for several days, nor did the addition of 3.0 g of DDI (equivalent to the dinitro-bis-phenol) assist the solution.

When 0.5 g of dinitro-bis-phenol-A was mixed with 2.0 g of polypropylene glycol (Dow D-1270) and heated to 100°C, much dissolved; however, most recrystallized upon re-cooling to 25°C.

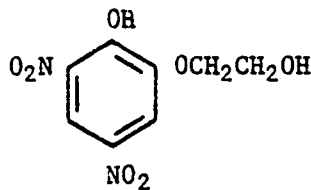
MISCELLANEOUS NITRATIONS

Nitration of bis-phenol-A [2,2-bis(4-hydroxyphenyl)propane] in benzene with 8N nitric acid at 20-25°C for 17 hr yielded mainly tri- and tetranitro compounds. For example, one fraction poorly soluble in both benzene and ethanol melted 220-230°C and had 12.82%N (theory for trinitro is 11.57% and for tetranitro is 13.73%). ^1H NMR (CDCl_3 plus $\text{DMSO}-d_6$, 60 MHz), δ 1.80 (s, 6H, CH_3), 8.17 (s, 4H, H_2 , H_6 , H_2' , H_6'). Another fraction, soluble in benzene but recrystallizable from benzene-cyclohexane, melted 135-140°C and contained 11.58%N by analysis. ^1H NMR (CDCl_3 , 60 MHz), δ 1.77 (s, 6H, CH_3), 7.10 (d, 1H, H_5 , $J_{\text{H}_5\text{H}_6} = 8.5$ Hz), 7.40 (dd, 1H, H_6 , $J_{\text{H}_5\text{H}_6} = 8.5$ Hz, $J_{\text{H}_2\text{H}_6} = \sim 2$ Hz), 8.10 (d, 1H, H_2 , $J_{\text{H}_2\text{H}_6} = \sim 2$ Hz), 8.20 (s, 2H, H_2' , H_6').

When the nitrating time was reduced to 1.5 hr at 22-25°C, the isolated crude product had a m.p. 110-120°C. The ^1H NMR spectrum indicated mainly the dinitro-derivative with some trinitro. The nitrogen analysis was consistent (found: 9.43%; theory for dinitro, 8.81%).

Nitration of 2,2'-dihydroxybiphenyl in benzene with 8N nitric acid gave a mixture of di- and trinitro compounds, m.p. 180-250°C, which were not soluble in DDI and only poorly soluble in THF.

2-(2-HYDROXY-3,5-DINITROPHENOXY)ETHANOL

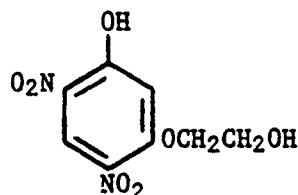


This compound was made in 64% yield (crude) when 30.8 g (0.2 mole) of 2-(2-hydroxyphenoxy)ethanol in 150 ml of benzene was nitrated at $25 \pm 2^\circ\text{C}$ with 95 ml of 6N nitric acid using 0.1 g of sodium nitrite as catalyst. About 1.25 hr were required for the addition of the acid to the vigorously stirred and cooled benzene solution. The product, which was a mixture of dark tar and orange solid, was recovered, washed well with water and dried. It was next extracted with eight 100 ml portions of boiling benzene; the combined extracts were evaporated to dryness and the residue recrystallized twice from 4:1 water-2-propanol and once from 2:1 water-2-propanol with charcoal decolorization; m.p. 152.5-155.5°C after vacuum drying. ^1H NMR (CDCl_3 plus $\text{DMSO}-d_6$; 60 MHz), δ 3.96 (t, 2H, $-\text{CH}_2-\text{OH}$), 4.26 (t, 2H, aryl- $\text{O}-\text{CH}_2-$), 7.95 (d, 1H, H_6 , $J_{\text{H}_4\text{H}_6} = \sim 2.5$ Hz), 8.53 (d, 1H, H_4 , $J_{\text{H}_4\text{H}_6} = \sim 2.5$ Hz).

Anal. Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_7$: C, 39.35; H, 3.30; N, 11.47. Found: C, 39.37; H, 3.33; N, 11.43.

An attempt to nitrate 2-(2-hydroxyphenoxy)ethanol with 3N nitric acid and sodium nitrite catalyst at 25-30°C was unsuccessful.

2-(3-HYDROXY-4,6-DINITROPHENOXY)ETHANOL

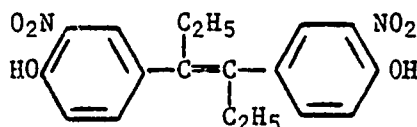


This compound, m.p. 88-89°C after recrystallization from benzene, was recovered in low yield from the nitration of 2-(3-hydroxyphenoxy)-ethanol in benzene with 3N nitric acid and sodium nitrite catalyst at 25-30°C. Much resinous material, melting above 320°C, was formed.

^1H NMR (DMSO- d_6 plus CDCl_3 , 60 MHz), δ 4.04 (t, 2H, $-\text{CH}_2\text{OH}$), 4.31 (t, 2H $\text{O}-\text{CH}_2\text{CH}_2\text{OH}$), 6.92 (s, 1H, H_2), 8.87 (s, 1H, H_5), 11.0-11.5 (broad s, 1H, phenolic-OH); the alcohol OH was buried under the AA'BB' pattern of the ethylene group.

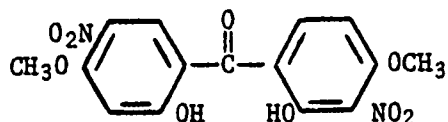
Anal. Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_7$: C, 39.35; 3.30; N, 11.48. Found: C, 39.73; H, 3.41; N, 11.24.

Based on an ^1H NMR analysis of a semi-solid residue obtained after isolation and recrystallization of the above dinitro compound, some mono-nitro compound was also formed (present in the spectrum was a doublet, $J = 10$ Hz, and a doublet of doublets, $J = 10$ Hz and $J = \sim 1$ Hz). No effort was made to recover and purify this mono-nitro compound and to ascertain whether it was the 4- or 6-isomer.



Diethylstilbesterol (16.8 g, 0.0625 mole) slurried in 150 ml of benzene was nitrated in the usual manner at 25-30°C with 85 ml of 3N nitric acid and 0.2 g of sodium nitrite; yield, 24.0 g of orange gum. Extraction with one 50 ml and three 25 ml portions of hot ethanol left 9.7 g of solid, m.p. 175-185°C, whose ^1H NMR indicated that it was largely the desired dinitro compound. ^1H NMR (DMSO- d_6 , 60 MHz), δ 0.72 (t, 3H, $-\text{CH}_2\text{CH}_3$), 2.15 (q, 2H, $-\text{CH}_2\text{CH}_3$), 7.20 (d, 1H, H_5 , $J_{\text{H}_5\text{H}_6} = 8.5$ Hz), 7.45 (dd, 1H, H_6 , $J_{\text{H}_5\text{H}_6} = 8.5$ Hz, $J_{\text{H}_2\text{H}_6} = \sim 1$ Hz), 7.74 (d, 1H, H_2 , $J_{\text{H}_2\text{H}_6} = \sim 1$ Hz).

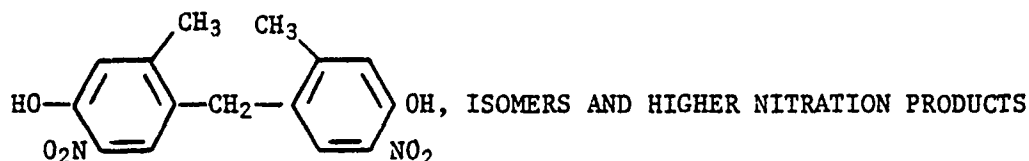
2,2'-DIHYDROXY-4,4'-DIMETHOXY-3,5'-DINITROBENZOPHENONE



This compound was isolated in about 5% yield from the mixture of products formed during the nitration of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone in benzene at 25-30°C with 4N nitric acid; m.p. 219.5-220.5°C after recrystallization from benzene and vacuum drying at 70°C, 25 mm to remove the half mole of solvate. ^1H NMR (CDCl_3 plus $\text{DMSO}-d_6$, 60 MHz), δ 4.02 (s, 6H, OCH_3), 6.81 (s, 1H, $\text{H}_{3'}$), 6.86 (d, 1H, H_5 , $J_{\text{H}_5\text{H}_6} = 9$ Hz), 7.79 (d, 1H, H_6), 8.10 (s, 1H, H_6').

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_9$: C, 49.46; H, 3.32; N, 7.69. Found: C, 49.48; H, 3.24; N, 7.53.

Probably because of the somewhat hindered position of the hydroxyl groups, this compound in THF reacted only very slowly with DDI (Thermolite #12 catalyst).

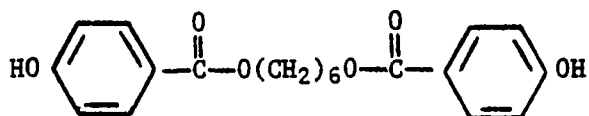


Meta cresol was condensed with formaldehyde following the procedure of Hardin and Reid.¹⁷

The crude product so obtained was nitrated in the usual manner in benzene at 20-25°C using 6N nitric acid; the nitration product was a viscous liquid. Small quantities of solid products, some melting up to 230°C, were recovered by digestion of the crude nitration product with hot 95% ethanol followed by cooling; but the bulk of the product, because of the complexity of the mixture, remained as a liquid. Both the ^1H NMR spectra and nitrogen analyses (10.2-10.9%) on the various fractions indicated mixtures of di- and trinitro bodies. The purified liquid mixture (tar removed by charcoaling) did not furnish a homogeneous system with DDI even upon warming; a mutual solvent, such as THF, was required.

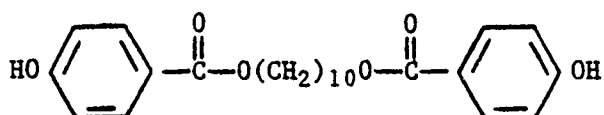
¹⁷ W. C. Hardin and E. E. Reid. "The Condensation of Certain Phenols With Some Aliphatic Aldehydes," *J. Am. Chem. Soc.*, Vol. 54 (1932), pp. 4325-30.

PREPARATION AND NITRATION OF ESTERS OF 4-HYDROXYBENZOIC ACID



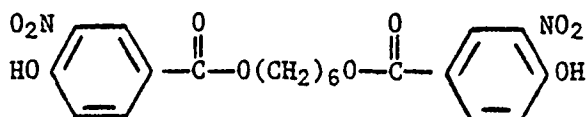
This diester was made by refluxing 4-hydroxybenzoic acid (11.0 g, 0.080 mole) and 1,6-hexanediol (4.5 g, 0.038 mole) in dry benzene with 0.4 g of 4-toluenesulfonic acid monohydrate until the theoretical amount of water was evolved; m.p. 179-181°C after recrystallization from absolute ethanol. ^1H NMR (CDCl_3 plus DMSO-d_6), δ 1.57 (broad s, 8H, 4CH_2), 4.30 (t, 4H, OCH_2 -), 6.90 (d, 4H, $\text{H}_3, \text{H}_3', \text{H}_5, \text{H}_5', \text{J} = 9 \text{ Hz}$), 7.97 (d, 4H, $\text{H}_2, \text{H}_2', \text{H}_6, \text{H}_6', \text{J} = 9 \text{ Hz}$).

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_6$: C, 67.02; H, 6.19. Found: C, 67.08; H, 6.50.



This compound was prepared as above except 1,10-decanediol was used. After two recrystallizations from absolute ethanol, the diester melted 158-161°C. ^1H NMR (CDCl_3 plus DMSO-d_6 , 60 MHz), δ 4.28 (t, 4H, $-\text{OCH}_2\text{CH}_2-$), 6.92 (d, 4H, $\text{H}_3, \text{H}_3', \text{H}_5, \text{H}_5', \text{J} = 10 \text{ Hz}$), 7.93 (d, 4H, $\text{H}_2, \text{H}_2', \text{H}_6, \text{H}_6', \text{J} = 9 \text{ Hz}$), 9.88 (s, 2H, $\text{HO}-$).

Anal. Calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_6$: C, 69.54; H, 7.30. Found: C, 69.54; H, 7.43



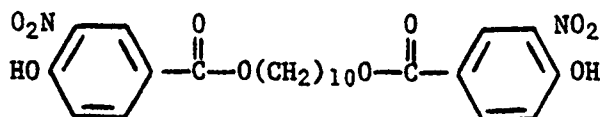
1,6-Hexanediol di-(4-hydroxy benzoate) (4.3 g, 0.012 mole) in 15 ml of 96% sulfuric acid was nitrated at 15-25°C with 2.5 g (0.025 mole) of 70% nitric acid during 45 min; quenched on ice, filtered, washed with water and dried, yield of crude product, 5.1 g, m.p. 140-165°C. Extraction of the crude product with two 150 ml and one 100 ml portions of boiling 95% ethanol left impure dinitro compound, m.p. 180-181°C.

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_{12}$: N, 6.25. Found: N, 6.52.

Cooling the alcoholic extracts furnished a pale yellow granular solid, m.p. 140-155°C.

Anal. Calcd. for $C_{20}H_{21}N_3O_{12}$: N, 8.52. Found: N, 8.50.

The starting unnitrated diester was recovered after an attempt to accomplish this nitration with 3N nitric acid and nitrite ion catalysis using the same procedure routinely used with the bis-phenol,



This dinitro-diester was made by the same procedure as in the previous experiment. The residue left after extracting the crude product with hot ethanol melted 132-134°C, or 135-137°C after allowing the melt to cool and resolidify, then remelting. This ester was readily soluble in tetrahydrofuran, poorly soluble in DDI, somewhat soluble in hot IDP but crystallized upon cooling, and poorly soluble in BDNPF/A. The 1H NMR spectrum was consistent with the assigned structure.

Anal. Calcd. for $C_{24}H_{28}N_2O_{10}$: N, 5.55. Found: N, 5.66.

Appendix C

MISCELLANEOUS PREPARATIONS

PREPARATION OF THE BIS-MALEIMIDE OF DIMER DIAMINE

This compound was prepared by dissolving 60.0 g (0.2 equivalent) of dimer diamine (General Mills) in 50 ml of 1,1,2-trichlorethane and 22.6 g (0.23 mole) of maleic anhydride in 125 ml of 1,1,2-trichlorethane. The system was swept with nitrogen and the dimer diamine solution added to the maleic anhydride solution dropwise, keeping the temperature below 35°C. After the addition was completed, stirring was continued for 1.0 hr. Magnesium acetate tetrahydrate, 4.29 g (0.02 mole), 49.0 g (0.48 mole) of acetic anhydride, and 42.5 g (0.42 mole) of triethylamine were added. The temperature was rapidly raised to 94°C, held at this temperature for 1 hr and then cooled to room temperature. The solvent was removed on a rotary evaporator. The crude product was dissolved in cyclohexane and washed twice with aqueous sodium chloride, centrifuging to break the emulsion. The product was washed with aqueous sodium hydroxide solution and then with water until free of base, and dried over anhydrous sodium sulfate. The solvent was removed and the product dried in a vacuum. The crude bis-maleimide was purified by column chromatography over Florisil and eluted with benzene.

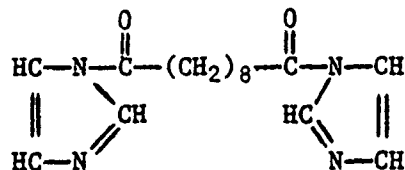
METHYL 4-IMIDAZOLECARBOXYLATE

This compound (m.p. 153-156°C) was made by refluxing diimidazo[3,4-a:3',4'-d]piperazin-2,5-dione in methanol, followed by two recrystallizations from ethanol. ¹H NMR (CDCl₃ plus DMSO-d₆, 60 MHz), δ 3.87 (s, 3H, $\text{O}-\text{CH}_3$), 7.73 (s, 2H, H₂, H₅). The diimidazo[3,4-a:3',4'-d]piperazin-2,5-dione, which behaves as the anhydride of 4-imidazole carboxylic acid, was made in low yield by the method of Kasina and Nematollahi¹⁴

4-Acetylimidazole, m.p. 171-173°C, after recrystallization from acetonitrile, was recovered as a by-product in this preparation of diimidazo[3,4-a:3',4'-d]piperazin-2,5-dione from 4,5-imidazole dicarboxylic acid. ¹H NMR (CDCl₃ + DMSO-d₆, 100 MHz), δ 2.39 (s, 3H, CH₃CO), 3.4 (broad s, 1H, NH), 7.65 (s, 1H, H₂ or H₅), 7.68 (s, 1H, H₅ or H₂).

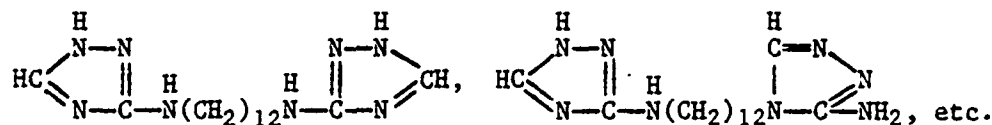
Anal. Calcd. for $C_5H_6N_2O$: C, 54.53; H, 5.49; N, 25.46; mol wt 110.1.
 Found: C, 54.29; H, 5.44; N, 25.33; mol wt (mass spec.), 110.

SEBACOYL BIS(1-IMIDAZOLE)



Sebacic acid (4 g) was dissolved in 100 ml of dry tetrahydrofuran and treated with 10 g of 1,1'-carbonyldiimidazole. There was a vigorous evolution of gas with warming; 100 ml more of solvent was added. Solid product soon separated; when the reaction was complete the product was removed, washed with solvent and dried.

N,N'-BIS(1,2,4-TRIAZOYL-3)-1,12-DIAMINODODECANE AND ISOMERS



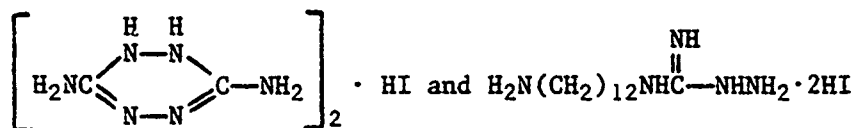
An impure mixture of isomers was made in low overall yield by the following series of reactions:

(1) One equivalent of 1,12-dodecanediamine was condensed with two equivalents of S-methyl-iso-thiosemicarbazide hydroiodide in absolute ethanol to form a di-aminoguanidine derivative. (2) The latter was converted to the 1,2,4-triazole derivatives by heating with excess 98% formic acid at 90-95°C for 4 hr. (3) The mixture was dissolved in water, made basic and the precipitated solid recrystallized from ethanol. A fraction, melting 226-231°C, was analyzed.

Anal. Calcd. for $C_{16}H_{30}N_8$: C, 57.45; H, 9.04; N, 33.50. Found: C, 57.03; H, 9.39; N, 32.91.

Although this material was poorly soluble in tetrahydrofuran, it did react slowly at 25°C with DDI when a slurry in this solvent was stirred vigorously. After five days a stiff gel was obtained. Removal of the solvent under vacuum at 70°C left a tough, rubbery product, which did not soften or melt at 145-150°C during 5 min.

3,5-DIAMINO-1,2-DIHYDRO-1,2,4,5-TETRAZINE HYDROIODIDE AND N-(AMINOGUANYL)-1,12-DIAMINODODECANE DIHYDROIODIDE

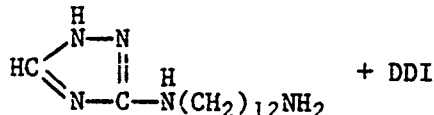


These two compounds were recovered, instead of the desired N,N'-di(aminoguanyl)-1,12-diaminododecane-bis-hydroiodide, in an experiment similar to the previous one when two molar equivalents of S-methyl-isothiosemicarbazide hydroiodide and one of 1,12-diaminododecane were reacted in absolute ethanol.

Anal. Calcd. for $\text{C}_4\text{H}_{13}\text{IN}_{12}$: C, 13.49; H, 3.68; I, 35.63; N, 47.20. Found: C, 13.57; H, 3.72; I, 35.81; N, 46.96.

The second compound melted broadly and indefinitely.

Anal. Calcd. for $\text{C}_{13}\text{H}_{33}\text{I}_2\text{N}_5$: C, 30.42; H, 6.48; N, 13.56. Found: C, 30.12; H, 6.37; N, 13.57; 13.69.



The N-(1,2,4-triazolyl-3)-1,12-dodecanediamine was made from N-(aminoguanyl)-1,12-dodecanediamine dihydroiodide (see previous experiment) and formic acid by a conventional procedure. After recrystallization from benzene, it was obtained as white, felted needles, m.p. 149.5-150.5°C.

Anal. Calcd. for $\text{C}_{14}\text{H}_{29}\text{N}_5$: C, 62.88; H, 10.93; N, 26.19. Found: C, 63.04; H, 10.84; N, 26.10.

When mixed with an equivalent amount of DDI and heated at 100°C for 1 hr, a homogeneous melt was not realized. After 2 hr at about 150°C, a gummy, rubbery, but non-liquid and still non-homogeneous, mass was formed.

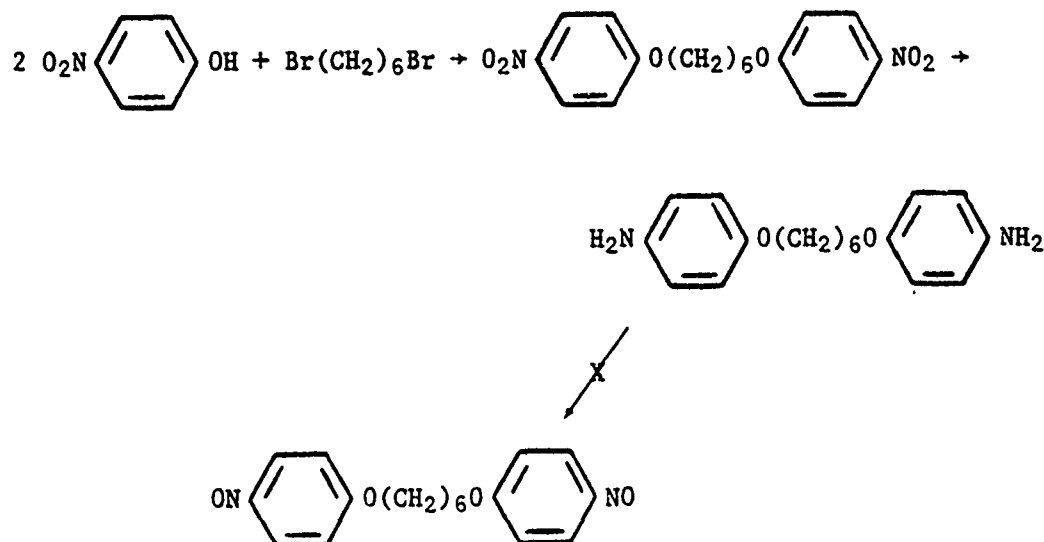
Appendix D

BIS-NITROSO COMPOUNDS

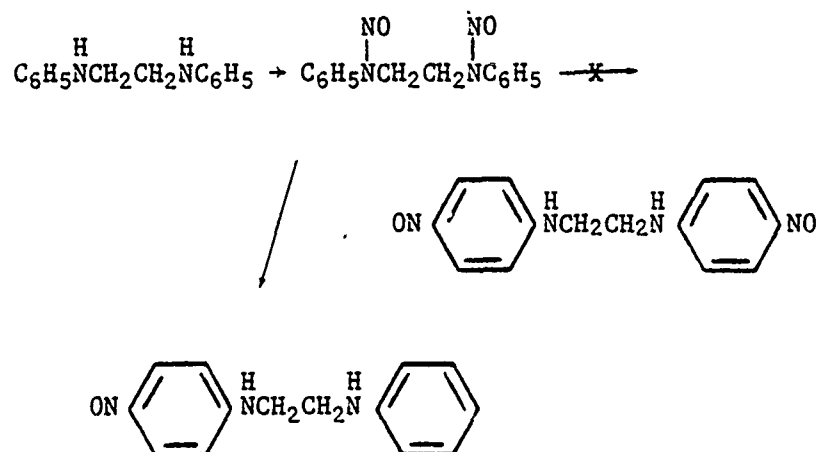
Nitroso compounds appeared to be candidate materials for the preparation of polymers which reversibly dissociate at elevated temperature. As referenced in the Introduction, nitroso compounds are known to enter into a Diels-Alder reaction with conjugated dienes and the adducts will dissociate at elevated temperature.

The aliphatic nitroso compounds exist as dimers unless a strong electronegative group is attached to the α -carbon. Likewise, aromatic nitroso compounds dimerize unless a strong electronegative group is attached to the ortho or para position of the aromatic ring. The nitroso dimer is a stable compound under normal conditions; however, they are known to dissociate into the respective nitroso compounds when heated at or near their melting points. In view of the above, attempts were made to prepare dinitroso derivatives for evaluation.

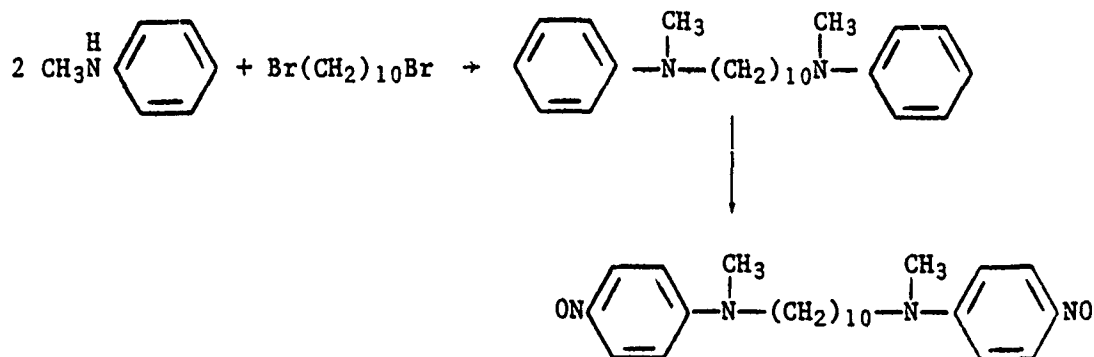
p-Butoxynitrosobenzene is reported to be soluble in aliphatic hydrocarbons. Therefore, attempts were made to prepare 1,6-bis(p-nitrosophenoxy)hexane and evaluate this compound as a curing agent for a diene terminated prepolymer. The route selected was to prepare 1,6-bis(4-nitrophenoxy)hexane by reacting p-nitrophenol with 1,6-dibromohexane. The dinitro compound was converted to the corresponding diamine by reduction in the presence of platinum oxide. All attempts to prepare the 1,6-bis(4-nitrosophenoxy)hexane resulted in hydrolysis of the ether linkage. Since the 4-nitrosophenylalkyl ethers are very unstable under both acidic and basic conditions, no further work was done with these compounds.



The N-alkylanilines can be nitrosated to form the N-nitroso derivatives. These compounds will undergo a Fischer-Hepp rearrangement producing the corresponding p-nitroso compound. Therefore, N,N'-dinitroso-N,N'-diphenyl-1,2-diaminoethane was obtained by nitrosating N,N'-diphenyl-1,2-diaminoethane. Rearrangement of the N,N'-dinitroso compound resulted in the formation of N-4-nitrosophenyl-N'-phenyl-1,2-diaminoethane in place of the desired N,N'-(4-nitrosophenyl)-1,2-diaminoethane.



The N,N-dialkylanilines can be nitrosated to form the corresponding 4-nitroso derivatives. Therefore, N-methylaniline was reacted with 1,10-dibromodecane to form N,N'-diphenyl-N,N'-dimethyl-1,10-diaminodecane. This compound was nitrosated to form N,N'-di(4-nitrosophenyl)-N,N'-dimethyl-1,10-diaminodecane.



In an effort to determine if the dinitroso compounds will produce a thermally dissociable polymer, the N,N'-di(4-nitrosophenyl)-N,N'-dimethyl-1,10-diaminodecane was mixed with a diene terminated prepolymer. No cure was obtained because the dinitroso compound was insoluble in the polymer.

The experimental work on the preparation of the dinitroso compounds has shown that these compounds are difficult to prepare; some were not stable and all were solids. They were insoluble in the prepolymers that are needed to produce an elastomeric binder. The results suggest that the dinitroso compound should be a relatively high molecular weight liquid so that when it dimerizes it will form an elastomer. Likewise, if it is to be reacted with a prepolymer, it should be a liquid that is miscible with the prepolymer or it should be soluble. The problems encountered with the solid dinitroso compounds suggest that it would be very difficult to prepare a high molecular weight liquid dinitroso compound. Therefore, it was the consensus that this area of investigation be abandoned.

1,6-BIS(4-NITROPHENOXY)HEXANE

A mixture consisting of 57.6 g (0.417 mole) p-nitrophenol, 48.8 g (0.2 mole) 1,6-dibromohexane, 57.22 g (0.207 mole) anhydrous potassium carbonate, 1.32 g (0.008 mole) potassium iodide and 280 ml of methyl-ethylketone was heated at 70°C for 72 hr with stirring. The reaction mixture was diluted with 200 ml of benzene and filtered. The filtrate was washed with water and the organic layer dried over anhydrous sodium sulfate. The residue was again extracted with benzene, which was also water washed and dried. The two benzene solutions were combined and the benzene removed on a rotary evaporator. The solid residue was recrystallized from ethanol-benzene (90:10). Yield: 41.5 g (57.6%). Melting point 105-106°C.

1,6-BIS(4-AMINOPHENOXY)HEXANE

1,6-Bis(4-nitrophenoxy)hexane (22.31 g, 0.062 mole) in 250 ml of absolute ethanol was hydrogenated over 0.50 g of platinum oxide at an initial pressure of 50 psig. The total pressure drop was 30.9 lb (theoretical 29.8 lb). The product was dissolved in hot ethanol and filtered to remove the catalyst. It was recrystallized from ethanol. Yield: 16.6 g (89.2%). Melting point 141-143°C.

N,N'-DIPHENYL-N,N'-DINITROSO-1,2-DIAMINOETHANE

N,N'-Diphenyl-1,2-diaminoethane (15.0 g, 0.071 mole) was suspended in 250 ml of water and 55 ml of concentrated hydrochloric acid and warmed with stirring until the amine dissolved as the hydrochloride. On cooling, the amine-hydrochloride formed a fine precipitate. A solution of 13.1 g (0.19 mole) of sodium nitrite in 60 ml of water was added dropwise to the amine-hydrochloride dispersion with stirring and maintaining the temperature at 0-1°C. The addition time was 0.75 hr. The stirring was continued an additional 2 hr, allowing the temperature to rise to 10°C. The nitroso compound was filtered and dried under vacuum. The crude product was recrystallized from benzene after decolorizing with Norit A. Yield: 14.6 g (75.9%). Melting point 161-163°C.

ATTEMPTED PREPARATION OF N,N'-BIS(4-NITROSOPHENYL)-1,2-DIAMINOETHANE

N,N'-Dinitroso-N,N'-diphenyl-1,2-diaminoethane (2.0 g, 0.007 mole) was suspended in 150 ml of dimethoxyethane and warmed to 36°C, with stirring, to dissolve the dinitroso compound. Methanol saturated with hydrogen chloride (30 ml) was added and the stirring continued for 3.5 hr allowing the temperature to drop to ambient. Ether was added to precipitate the dissolved product, which was then filtered. The residue was suspended in water and made basic using ammonium hydroxide. The product was extracted into ethylene dichloride which was dried over anhydrous sodium sulfate. After removing the solvent on a rotary evaporator, the product, N-4-nitrosophenyl-N'-phenyl-1,2-diaminoethane, was recrystallized from benzene-heptane and formed metallic blue-black crystals. Yield: 0.2 g. Melting point 147-149°C (dec.). Observed MW (VPO): 240.06. Theoretical MW for N-4-nitrosophenyl-N'-phenyl-1,2-diaminoethane: 240.16. Theoretical MW for N,N'-bis(4-nitrosophenyl)-1,2-diaminoethane: 270.17.

N,N'-DIPHENYL-N,N'-DIMETHYL-1,10-DIAMINODECANE

N-Methylaniline, 32.14 g (0.3 mole), 1,10-dibromodecane, 30.0 g (0.1 mole), potassium carbonate, 41.5 g (0.3 mole) and 150 ml of water

were heated at 85°C, with stirring, for 27 hr. The organic layer was separated and stirred with 17.2 g (0.43 mole) sodium hydroxide in 150 ml water. Benzenesulfonyl chloride (35.2 g, 0.2 mole) was added dropwise over a period of 0.75 hr, then stirred for an additional 0.75 hr. The excess sulfonyl chloride was hydrolyzed by warming for 0.5 hr. The solution was made acid, and benzene extracted to remove any N-methyl-N-phenyl-benzenesulfonamide. The aqueous phase was centrifuged to clarify. The aqueous layer was basified with ammonium hydroxide and the product extracted into benzene, which was dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to leave a light yellow oil. Yield: 31.29 g (88.9%).

N,N'-DI(4-NITROSOPHENYL)-N,N'-DIMETHYL-1,10-DIAMINODECANE

A solution of 3.52 g (0.01 mole) of N,N'-diphenyl-N,N'-dimethyl-1,10-diaminodecane in 21.0 g (0.35 mole) of glacial acetic acid, 5.0 ml concentrated hydrochloric acid (0.06 mole) and 50 ml of water was cooled to 0-1°C. With stirring, 2.76 g (0.04 mole) of sodium nitrite in 7.0 ml of water was added dropwise to the diamine solution, keeping the temperature below 4°C. The addition time was 5 min; stirring was continued for 1.0 min. The red reaction mixture was immediately poured into a rapidly stirred solution of 47.5 g (0.6 mole) ammonium carbonate in 400 ml water using caution to prevent frothing out of the beaker. The solution turned a dark green. The product was extracted into 250 ml of ethylene dichloride and dried over anhydrous sodium sulfate. The ethylene dichloride was removed on a rotary evaporator and the residue recrystallized from 2-propanol. The dinitroso compound separated as fine dull green crystals. Yield: 2.0 g (48.5%). Melting point 103-104°C. MW: Theoretical: 410.24; observed (VPO): 411.64.

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NOMENCLATURE

Bis-phenol-A	2,2-Bis-(4-hydroxyphenyl)propane
Bis-phenol-B	2,2-Bis-(4-hydroxyphenyl)butane
BDNPF/A	Bis-dinitropropyl formal/acetal
DABCO	Triethylene diamine
DDI	Dimer diisocyanate -- General Mills
Desmodur N-100	A triisocyanate from Mobay
HDI	1,6-Hexamethylene diisocyanate
IDP	Isodecyl pelargonate
LDIM	Lysine diisocyanate methyl ester
Thermolite #12	Dibutyltin dilaurate
THF	Tetrahydrofuran

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