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NERVA FUEL ELEMENT DEVELOPMENT PROGRAM SUMMARY REPORT - JULY 1966 THROUGH JUNE 1972

Carbons Derived from Organic Compounds

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NERVA FUEL ELEMENT DEVELOPMENT PROGRAM SUMMARY REPORT - JULY 1966 THROUGH JUNE 1972

Carbons Derived from Organic Compounds

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Date Issued - February 3, 1973

This report presents a summary of the work that was performed on carbon precursors for NERVA fuel elements for the Space Nuclear Systems Office, under Purchase Orders SNC-51, SNC-73, SNC-81, and SNC-95 during the period July 1966 through June 1972.

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Prepared for the U.S. Atomic Energy Commission
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ABSTRACT

This phase of the NERVA program was established to design, procure, develop, and evaluate precursor systems that would allow controlled production of filler and binder graphite, and that would, in combination, allow the production of high coefficient-of-thermal-expansion graphite fuel elements. Filler/binder precursor systems were developed from isotruxene, cinnamylideneindene, acenaphthylene, and commercial petroleum pitches.

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FOREWORD

The NERVA graphite fuel element program, which was funded for several years by the Space Nuclear Systems office (SNSO), has been terminated. This report, abstracted from a series of progress reports which were routinely issued during the course of the fuel element studies, summarizes the information that was collected during the binder and filler studies. This study was initiated to investigate the use of organic compounds in an endeavor designed to obtain repeatable and reliable precursor raw materials for the NERVA program.

SUMMARY

An effort was made to develop reproducible carbon precursor systems from simple organic compounds. Precursor systems were developed from indene (C_9H_8) and acenaphthylene (ACN, $C_{12}H_{18}$), and were evaluated for both filler and binder applications.

Two candidate materials derived from indene were isotruxene (ITX, $C_{27}H_{18}$) and cinnamylideneindene (CAI, $C_{18}H_{14}$). Coke yields of these two materials were dependent on the method of polymerization, and ranged from 40 to 70 percent. In the polymer form, both were amenable to binder applications. Likewise, both materials could be used to produce filler carbon ranging in crystallinity from amorphous to anisotropic; and, thus included the production of a fine-grain, isotropic carbon.

Polymer products derived from acenaphthylene were evaluated as candidate binders. Coke yields of these materials ranged from 40 - 60 percent, and were dependent on the method of polymerization. Binders that were fluid at room temperature were developed by adding isotruxene and indene as diluents.

Two additional binder candidates consisted of samples of a commercial petroleum pitch. These materials were found to be soluble and low melting, and suitable for binder applications. Coke yields ranged from 40 - 55 percent, and the derived graphites were highly anisotropic. Crystallinity of the derived carbons was modified by the inclusion of specific additives.

INTRODUCTION

A major part of any fabrication program is to certify the materials and procedures relative to a set of specifications. Thus, of vital interest to the fabrication engineer are the reproducibility of materials and their adaptation to reproducible fabrication schemes. For complex materials and sophisticated designs, rarely would a single property serve as an acceptable measure of reproducibility; but, rather, a combination of several properties would be required. The latter case exists for carbon precursor materials and is especially appropriate for petroleum and coal-tar products. In theory, the simpler the material the more easily it would be to characterize and certify that material. The ultimate goal would be a monomer material which could be certified and, subsequently, polymerized and pyrolyzed under controlled and reproducible conditions. Interest in such an approach has motivated this search for simple carbon precursors which would have the following characteristics: (1) readily available, (2) easily characterized and certified, (3) adaptable to controlled polymerization, (4) have high weight and volume yields on pyrolysis, (5) be precursors to both filler and binder carbon, and (6) allow controlled modifications of properties of derived carbon.

The current study was primarily concerned with developing precursor systems meeting some or all of these criteria and consisting of an evaluation of both synthetic and natural materials. Though termination of the program prevented the full realization of the initial goals, considerable progress was made toward those objectives, and the accumulated technology should add to the general understanding of carbon materials.

A summation report on one other phase of the NERVA program is entitled *NERVA Fuel Element Development (Precursor Carbon and Molded Graphite Studies)*, Y-1857.

STUDY OF THE CARBONS FROM ORGANIC COMPOUNDS

ACCOMPLISHMENTS

Procedures were developed for synthesizing numerous precursor materials derived from indene. Preparative procedures for two of the materials, isotruxene (ITX) and cinnamylideneindene (CAI), were scaled up to permit the production of 10 and 30-pound batches, respectively. These two materials were characterized with respect to their monomer, polymer, and carbon properties. Gel permeation chromatography was found to be a useful tool to determine the monomer content of these materials in the as-prepared form. Polymerization reactions of these two materials were studied extensively and furnished considerable correlation between their polymer properties and polymerization conditions. ITX was thermally stable under inert atmospheres at temperatures up to 300° C, but underwent slow polymerization at these temperatures in the presence of air or oxygen gas. Thus, ITX polymers were characterized as a function of the heat-treatment conditions, and appropriate procedures for converting ITX into a synthetic pitch were determined. Such pitches melt between 130 and 160° C and are readily soluble in hydrocarbon solvents.

By contrast, CAI polymerizes rapidly on melting (~ 190° C) without the presence of additives; and, thus, was studied extensively under autoclave conditions. Methods were developed for converting CAI into a soluble synthetic pitch melting at 50 - 75° C. Both of these synthetic pitches are useful in binder applications.

In addition, both CAI and ITX were evaluated as filler candidates, and both show potential for producing filler carbon. By including certain additives to promote crosslinking during polymerization, controlled modifications of properties of the carbon derived from both precursor systems were possible, allowing production of a fine-grain, isotropic carbon for fabricating high CTE graphites.

An additional synthetic precursor, acenaphthylene (ACN), was procured for polymerization studies and binder applications. Like CAI, ACN polymerizes on melting (~ 100° C) and its polymer properties were studied as a function of the heat-treatment conditions in an autoclave. Conditions for converting ACN into a soluble synthetic pitch (MP, 50 - 75° C) were determined. Both monomer and polymer ACN were evaluated as binder materials both with and without other precursor additives.

Two samples of a commercial petroleum pitch (from Ashland Oil) were evaluated as potential binder and filler materials. Though only partially characterized when the program was terminated, the pitch samples appeared quite amenable to binder applications due to their high solubilities and low softening points. A more extensive evaluation of these pitches consisted of blending them with various furan polymers to modify the properties of the derived carbons. Some of these mixtures showed considerable promise as binder materials as well as precursors to filler carbon with a variety of available structures.

DISCUSSION

This report will document, in a summary fashion, the work performed on carbon precursors and provide references to more detailed documentation elsewhere. Included in this

discussion will be studies of source, characterization, polymerization, carbonization, and utility of a selected number of precursor materials either obtained commercially or synthetically derived during the program. Commercial materials included petroleum pitches, furans, and polynuclear aromatic compounds while synthetic materials were largely derived from indene (C_9H_8).[1] Only part of a larger list[2] of these synthetic derivatives will be discussed in this report.

Materials which constituted a major portion of the study are listed in Table 1 along with their polymer and carbon properties.

Table 1

PROPERTIES OF CANDIDATE PRECURSOR MATERIALS

Precursor Material	Melting Temperature (° C)	Coke Yield at 1,000° C (%)	Carbon Properties after 2,800° C		
			d_{004} (A)	g Factor[1]	L_c (A)
ITX	210 - 220	45	1.7025	0.41	97
ITX-Pitch[2]	130 - 160	73	1.6828	0.88	227
CAI	172 - 190	40	1.6820	0.89	281
CAI-Pitch 300[3]	50 - 75	46	1.6825	0.88	265
CAI-Pitch 340[4]	40 - 75	47	1.6822	0.89	331
ACN	85 - 88	30	1.6797	0.94	704
ACN-Pitch 300[3]	45 - 50	50	-	-	-
ACN-Pitch 340[4]	55 - 65	37	-	-	-
A-240 Pitch[5]	116[6]	52	1.6810	0.91	240
A-170 Pitch[5]	77[6]	39	1.6805	0.92	343

(1) $d_{002} = (g)(3.355) + (1-g)(3.44)$. From Maire and Mering.[3]
(2) As prepared by Method A, Appendix D.
(3) Prepared by autoclave treatment at 300° C.
(4) Prepared by autoclave treatment at 340° C.
(5) Samples of petroleum pitch from the Ashland Oil Company.
(6) Ring and ball softening points, furnished by Ashland Oil.

Isotruxene (ITX)

Source - Isotruxene ($C_{27}H_{18}$) is a trimeric derivative of indene that was prepared synthetically by two procedures. The material can be prepared[4] in a relatively pure form (~ 85% ITX—the balance, indene polymers)[5] by an extended reflux reaction of mixtures of indene, 1,4-naphthoquinone, and N,N,N′,N′-tetramethyl-1,3-butanediamine (TMBDA) in a weight ratio of 100:10:1, respectively (see Appendix A). No problems were encountered in scaling up this procedure from 3-liter reactors to 10-gallon reactors with the latter yielding approximately 10 pounds of product per batch.

A second procedure[6,7] involved a short-time autoclave treatment (250° C, 300 psi) of indene alone to yield an isotruxene/truxene (TX) mixture containing approximately 60 percent ITX (see Appendix B). Separation of these isomers can be achieved by solvent extraction,[8] although considerable potential has been shown for adapting ITX/TX blends to precursor applications.[9]

Characterization - ITX is a highly crystalline compound and thus has a high melting point (210 - 220° C),[4] and is soluble only in hot aromatic hydrocarbon solvents.[10] Characterization[4] of ITX was accomplished by using its melting properties, by infrared spectrophotometry, by mass analysis, and by molecular weight and distribution studies (see Appendix C). Gel permeation chromatography (GPC) was used to monitor the ITX products formed under reflux conditions and allowed an estimation of the ITX content in the products. Compositions of ITX/TX mixtures formed in autoclave reactions were determined by ultraviolet (UV) spectrophotometry.[11]

Polymerization - During polymerization, the crystalline ITX product is converted to a pitch of reduced crystallinity and melting point (130 - 160° C), and of greatly increased solubility.[12,13] Polymerization of ITX does not occur by classical radical-induced olefinic-type mechanisms; but, rather, requires oxidative conditions at elevated temperatures. Thus, ITX heated in the presence of air or oxygen at 250 - 300° C is converted to a pitch material (see Appendix D). Characterization of the polymers was achieved through molecular weight and distribution studies, mass analysis, and the pitch melting point.[14] The latter property was considerably dependent on the heat-treatment time and describes a minimum for intermediate times. Thus, melting properties were used to monitor the pitch products formed from ITX.

Binder Studies - ITX pitch may be used in binder applications either in molten form (~ 180 - 200° C) or as a room-temperature fluid after the addition of certain diluents. The latter formulations received considerable attention as binders for fuel-element fabrication. Greatest emphasis was given to the formulations of ITX, ACN, and indene (see Appendix E).[15] Viscosities of these formulations were studied as a function of composition and blending conditions. Blending conditions were found to be critical to viscosity control since ACN polymerized at blending temperatures (> 160° C), and the viscosity of the resulting formulations were significantly influenced by the degree of polymerization.

An alternate procedure which helps to circumvent this problem is suggested later (see **Binder Studies**, Page 12).

Carbonization/Graphitization - The coke yield and carbon properties of ITX are significantly influenced by the degree of oxygen-induced polymerization prior to carbonization. Coke yields of as-prepared isotruxene are typically 40 - 45 percent,[16] while those of ITX pitch are higher, and are dependent on the heat-treatment time and temperature conditions.[17] Carbon yields from ITX pitch prepared by the procedures in Appendix D are typically 60 - 70 percent.[18]

In addition to differences in coke yields, properties of the carbon after graphitization (2,800° C) are very much influenced by the polymerization conditions. ITX without oxygen-induced polymerization yields a carbon (after 2,800° C) with a very fine-grain

isotropic microstructure and a low order of crystallinity,[16] while that with the initial polymerization treatment is a large-grain, somewhat heterogeneous crystalline carbon.[18] The crystallinity of ITX-derived carbon as a function of the polymerization conditions was studied extensively.[17] Likewise, the crystallinity of ITX-derived carbon was studied as a function of the firing temperature in the range from 1,000 to 2,800° C.[19]

Filler Studies - Included in this study was a general evaluation of the methods which might be used to vary the crystallinity of ITX-derived carbon in a uniformly controlled and reproducible fashion, with a goal of producing a fine-grain, isotropic, high-CTE graphite. The approach consisted primarily of blending additives to ITX to induce changes in the carbon properties, and the uniformity of carbon from such blends is dependent on the miscibility of the mixture components during polymerization and/or carbonization. Mixtures which received greatest emphasis are discussed in the paragraphs that follow.

> **ITX/PMDA (pyromellitic dianhydride)** - The addition of PMDA to ITX produces two different effects in the crystallinity of the ITX-derived carbon that were a function of the PMDA concentrations.[20] At lower PMDA concentrations (< 20%), crystallinity increased, while higher PMDA concentrations resulted in decreased crystallinity. Thus, the crystallinity of carbon derived from this precursor blend can be controlled over a wide range by controlling the composition.
>
> **ITX/ITX Pitch** - As previously stated, ITX produces carbon which varies in crystallinity as a function of the degree of oxygen-induced polymerization prior to carbonization. As a result, controlled modification of derived carbon is possible by controlling the temperature/time conditions during the polymerization. However, a more easily controlled procedure involved blending ITX with an ITX pitch polymer.[21] In the latter case, crystallinity of the derived carbon is a function of composition.
>
> **TX/ITX Pitch** - TX yields a noncrystalline form of carbon,[22] and was thus observed to modify the crystallinity of ITX-derived carbon when blended in concentrations of up to 50 percent.[9] Higher TX concentrations result in a noncrystalline carbon. Coke yields of these mixtures were quite good (70 - 80%), and carbon crystallinity was observed to vary with the precursor composition.

Cinnamylideneindene (CAI)

Source - CAI ($C_{18}H_{14}$) is a condensation product of the reaction between indene and cinnamaldehyde, and it was produced, inhouse, during the program by the room-temperature reaction of these materials in methanol solutions containing a strong base (see Appendix F).[23] The preparative procedure was scaled up to 50-gallon reactor vessels from which product yields of 30 pounds were obtained. Products were typically 95 percent CAI; the remainder were primarily secondary organic products.[24]

Characterization - CAI is an orange-colored crystalline compound that melts at 172 - 190° C in the crude, as-prepared form. The monomer form of CAI has limited solubility at 25° C, but is quite soluble in hot hydrocarbons. CAI was characterized by its melting properties, by mass analysis, by molecular weight and distribution studies, and by spectrographic analysis.

GPC analysis was used to determine the CAI monomer content of the product,[25] and X-ray fluorescence was used to determine the residual potassium content.[26] The latter additive was introduced during the preparation step using potassium hydroxide as the reaction promoter. It was reduced to low levels (100 ppm) by repeated washing of the product in methanol or methanol/acetic acid mixtures.[26] Thus, the residual potassium content was a function of the washing procedure.

Polymerization - CAI is quite sensitive to polymerization reactions and can be catalytically polymerized while in solution or can be thermally polymerized at or near its melting temperature (~ 190° C).[27] Thermal polymerization reactions of CAI were studied extensively in this program and consisted primarily of autoclave reactions over the temperature range of 200 - 340° C.[28] Nominal pressures between 300 - 1,000 psi were used during these studies.

Autoclave polymerization converts CAI to an amorphous, low-melting (50 - 75° C), soluble polymer. Specific properties of these polymers are a function of the polymerization time and temperature; and, thus, some control over polymer properties can be obtained by controlling the heat-treatment conditions. The polymer forms of CAI are much more amenable to processing than the higher-melting, crystalline monomer.

Binder Studies - Properties of CAI polymers make these materials suitable binder candidates for extrusion, molding, impregnation, and other processes. The polymeric CAI may be blended with diluents for room-temperature processing or they may be used without dilution at elevated temperatures (~ 100° C). Binder formulations incorporating polymeric CAI and indene were studied as to viscosity and composition. Additional formulations incorporated polymeric CAI, acenaphthylene, and indene.

Carbonization/Graphitization - Coke yields of monomeric CAI are typically 40 percent,[26] while those of polymeric forms are equal or greater, and are somewhat dependent on the polymerization conditions.[29] After 2,800° C, CAI-derived carbon is quite crystalline and has a course-grain microstructure. Little or no difference was noted in the crystallinity of carbons derived from monomer and polymer materials. However, a factor that very significantly influenced the carbon properties was the content of residual potassium in the monomer prior to the polymerization and carbonization steps.[26]

Filler Studies - A large number of candidate precursors to filler carbon can be derived from CAI by blending specific additives. Some of these are presented in the paragraphs that follow.

> **CAI/Potassium** - Potassium has a significant effect on the properties of CAI-derived carbon and can thus be used to control the crystallinity of carbon for those applications which would not prohibit potassium contamination.[26,30] Carbon crystallinity decreased as the potassium content (either as the hydroxide or acetate) in the precursor increased, and a noncrystalline form of carbon results when potassium concentrations in the precursor exceed 5,000 ppm (0.5%). The potassium is equally effective when it is a residue or when added.

CAI/PMDA - The addition of PMDA to the CAI monomer results in a decrease in the crystallinity of derived carbon, and yields a noncrystalline carbon at PMDA concentrations greater than 20 percent.[31] In general, PMDA in concentrations up to 60 percent also enhances the coke yield of CAI. This system affords a variety of carbon structures that are a function of the composition.

CAI/XYN (p-xylylideneindene) - XYN, an indene derivative[32] that yields a noncrystalline carbon, can be added to the CAI monomer to decrease the crystallinity of the derived carbon. XYN concentrations above 60 percent result in a noncrystalline carbon. This hydrocarbon precursor system allows coke yields of 45 - 55 percent and produces carbon that is quite uniform in properties.

CAI/FAI (α-furfurylideneindene) - FAI, an oxygen-containing compound produced by the reaction of indene with furfural, yields a noncrystalline carbon and can be used successfully to modify the crystallinity of CAI-derived carbon. Addition of FAI to CAI monomer results in a decrease in the carbon crystallinity, and FAI concentrations above approximately 60 percent produce noncrystalline carbon. Coke yields of this precursor system are 35 - 50 percent, and the microstructures of the resulting carbons appear to be homogeneous.

Acenaphthylene (ACN)

Source - Most of the ACN ($C_{12}H_8$) used in the program was procured commercially (from Henley and Co) under specifications of 95 percent purity with no more than 500 ppm of total inorganic impurities.

Characterization - Studies of as-received ACN consisted of efforts to certify the materials, and were thus directed at determining and identifying the impurities. Common impurities in ACN were reduced (acenaphthene) and oxidized (acenaphthenone) forms of ACN.

ACN is a yellow crystalline compound that melts at approximately 85° C, and is quite soluble in hydrocarbon solvents.

Polymerization - ACN polymerizes readily when heated above its melting temperature (~ 95° C) and can thus be readily converted to a polymer resin.[33 - 35] However, polymers formed under these conditions tend to decompose back to acenaphthylene/acenaphthene monomer materials at approximately 300° C. Thus, greater attention was given to autoclave polymerization of ACN.[36] Polymerization was studied as a function of temperature (150 - 340° C) and time. When measured as a function of temperature, most ACN polymer properties had maxima or minima values for an autoclave temperature of approximately 300° C. In general, these polymeric materials are low melting (50 - 75° C) and quite soluble.

Binder Studies - ACN monomer is added as a diluent in ITX/ACN/indene binder formulations. Under the required blending conditions, some of the ACN polymerizes; and, in fact, seems to enhance the lubricity of the binder. However, control of the degree of polymerization is difficult. An alternate means of formulating this binder would be to add prepolymerized ACN in the quantity appropriate for the desirable properties which would, in turn, drop the fluid temperature of the blend such that the necessary ACN monomer

could be added at lower temperatures ($< 160^{o}$ C). Such formulations were studied as to viscosity, ACN polymer content, and total composition.

For elevated-temperature processing ($\sim 100^{o}$ C), the ACN polymers may be used without the addition of diluents.

Carbonization/Graphitization - Properties of ACN-derived carbon seem not to be very sensitive to polymerization conditions. ACN yields a highly crystalline carbon, and the crystallinity of carbon derived from monomer and polymer materials was quite similar. However, coke yields are influenced by polymerization conditions, and tended to be higher for autoclave polymerized materials than those obtained for the ACN monomer.

Filler Studies - ACN-derived carbon is a highly crystalline, coarse-grained graphite, and would tend to produce highly oriented structures when used as a filler carbon. Efforts to modify the properties of ACN-derived carbon were only partially successful and consisted of the addition of secondary components, as was discussed for CAI and ITX. Therefore, this material received less emphasis as a filler candidate than did the other precursor systems.

Petroleum Pitch

Source - Samples of a commercial petroleum pitch (from Ashland Oil) were received and evaluated during the latter part of the program. Ashland designations for the two materials receiving the greatest emphasis are A-170 and A-240, with the number denoting the softening point (in ^{o} F) of the pitch. These pitches are not residuals but are obtained as fractions during a distillation process.

Characterization - While these pitches had not been completely characterized at the close of the program, they were found to have a very low ash content (0.1 - 0.2%). The sulfur content of the samples was also fairly low (0.8 - 1.2%). Ashland has a process for desulfurization and has supplied samples of pitch containing approximately 0.1 percent sulfur. In addition to decreasing the sulfur by a factor of ten, the desulfurization step decreases the ash by a similar factor and renders it negligible. Both pitch materials are quite soluble in hydrocarbon solvents.

Binder Studies - Low softening points and high solubility make these two Ashland pitches amenable to binder applications either as molten materials at elevated temperatures or with diluents for room-temperature applications. Their utility as binder impregnants is enhanced by a high order of thermal stability at temperatures from 200 to 250° C.

A series of binders incorporating Ashland pitch were prepared by blending the pitch with furan materials in formulations largely suggested by the Quaker Oats Co. The suggestions were based on their knowledge of the furan components and the data from an earlier iteration of the binders that were formulated by Quaker Oats and evaluated at the Oak Ridge Y-12 Plant. The pitch/furan formulations were fluid at room temperature and covered a wide range of viscosities and carbon properties.

Carbonization/Graphitization - Both the A-170 and A-240 petroleum pitches yield carbons that have a high order of crystallinity, approaching that of ACN-derived carbon. As would

be expected from the softening point/molecular weight differences, coke yields of the A-240 pitch (50%) are higher than that of the A-170 pitch (40%).

Filler Studies - The Ashland petroleum pitches produce highly crystalline carbon; and, as such, were not considered as candidates for high-CTE filler for extruded carbon. However, modifications of this carbon were evident on the addition of furan materials; and, as a result, some of the pitch/furan mixtures have potential as filler materials for high-CTE applications.

CONCLUSIONS AND RECOMMENDATIONS

This study shows the potential of using simple organic compounds to develop precursor systems, and indicates the correlations that can exist between precursor properties, processing conditions, and carbon properties. The versatility that can be built into these systems is suggested by the marked influence that precursor chemistry and polymerization conditions have on the properties of derived carbon. This same observation would become a liability for precursor systems not subject to raw material and/or processing controls. To a large degree, available precursor systems based on natural sources fit into the latter category, and the inability to produce controlled carbon is one factor preventing carbon from receiving due consideration as a structural material. It would seem to suggest that the solution to the problem lies in the relationships to be found between precursor chemistry, polymerization mechanisms, and carbon properties. If so, polymer chemistry must become an integral part and vanguard of carbon technology if the full potential of carbon as an advanced engineering material is to be realized.

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APPENDIX A

PREPARATIVE PROCEDURE FOR ISOTRUXENE BY REFLUX REACTION

Typical procedure for a 10-gallon reactor.[4]

Expected product yield approximately 10 pounds.

1. **Formulate the Reactant Solution**

Reactant Quantities

Indene	22.2 kg or 22.2 l
1,4-naphthoquinone	2.2 kg
TMBDA (N,N,N',N'-tetramethyl-1,3-butanediamine)	220 cc

Reactor Design

A reactor vessel capable of attaining a temperature of 200° C was equipped with a motor-driven agitator, a condenser with a Dean-Stark-type trap to collect water, a thermocouple for monitoring the temperature, and valving to allow an inert gas sweep to exit through the condenser.

Formulation Procedure

Add indene to the reactor; initiate stirring. Add powdered 1,4-naphthoquinone and continue to stir for 15 to 30 minutes after addition. Add TMBDA.

2. **Heating Procedure**

Heat the reactor rapidly to the indene reflux temperature (~ 180° C). Continue the heating period for 24 to 30 hours.

3. **Work-Up Procedure**

Note: Work up can be done in reactors if appropriate in size and design; or reaction may be transferred while hot (~ 100° C) to work-up vessels.

Allow contents to cool to ambient temperature. Add an equal volume of methyl ethyl ketone (MEK) and agitate well for 15 minutes.

Filter the precipitate and wash well with fresh MEK. Product may be dried at 80 - 100° C.

4. Product Description

Product will be yellow-gold in color and will melt between 210 and 220° C (theoretical, 223° C). Approximately 25 percent of the starting indene is isolated as isotruxene.

5. Analytical Procedures

GPC was used to monitor the ITX products for organic impurities which appear as a secondary band. Products are typically 80 to 85 percent ITX.

APPENDIX B

PREPARATIVE PROCEDURE FOR ISOTRUXENE/TRUXENE MIXTURES BY AUTOCLAVE REACTIONS[6,7]

1. Reaction Procedure

Indene was placed in an autoclave and heated under static conditions at 250° C (initial nitrogen pressure of 300 psi) for 1 to 2 hours.

2. Work-Up Procedure

On cooling to ambient, an equal volume of MEK was added to the reaction mixture. After stirring for 15 minutes, the insoluble product was collected by filtration and washed with MEK. Product may be dried at 80 - 100° C. Approximately 25 percent of the indene is converted to truxene/isotruxene.

3. Analytical Procedure

The isotruxene content in the product was determined by ultraviolet spectrophotometry and was typically 60 percent ITX.

APPENDIX C

ANALYTICAL PROCEDURES USED IN CHARACTERIZING PRECURSOR SYSTEMS

Character	Analytical Procedure
Melting Point	Visual
Viscosity	Brookfield Continuous Recording Viscometer
Average Molecular Weight	Vapor-Pressure Osmometer
Molecular Weight Distribution	Gel Permeation Chromatograph
Mass Analysis	Mass Spectrophotometer
Oxygen	Neutron Activation
Nitrogen	Neutron Activation
Carbon/Hydrogen	Carbon Train
Sulfur	Parr Bomb
Inorganic Constituents	Ash, Semiquantitative Spectrograph
Structure Analysis	Nuclear Magnetic Resonance Spectroscopy Infrared and Ultraviolet Spectrophotometry
Thermal Analysis	Differential Thermal and Thermogravimetric
Coke Yield	Calculated from Residue in 3-Inch-High/ 3-Inch-Diameter Carbon Crucible after Cam-Controlled Heating Cycle of 48 Hours to 900° C
Carbon Properties	
Crystallinity	X-Ray Diffraction
Density	Helium Displacement
Surface Area	Nitrogen Adsorption

APPENDIX D

PREPARATION OF ITX PITCH

Method A[13]

ITX in bed depths (when molten) of 3/4 inch was heated in an air-circulating oven at 300° C for approximately 40 hours. Such a pitch melts over the range 130 - 160° C. Melting-point data were used to check the reproducibility of this procedure (heating times required to give this pitch vary with the bed depth and air flow).

Method B

ITX (20 kgs) was placed in a 10-gallon reactor equipped with motor-driven agitation and was heated at 300° C with air bubbling through the molten material. Heating times of 45 - 50 hours were required to produce a pitch having a melting point of 130 - 160° C (again heating times vary with the air flow rate and quantity of material).

APPENDIX E

FORMULATION OF ITX/ACN/INDENE BINDER

ITX pitch (see Appendix D) is heated to the molten state (~ 200° C) and an equal weight of ACN is added with stirring at 160 - 180° C. This mixture is allowed to cool to approximately 100° C and indene is added with stirring. The binder viscosity can be varied by varying the indene content.

APPENDIX F

PREPARATIVE PROCEDURE FOR CINNAMYLIDENEINDENE (CAI)

Typical Procedure for a 50 - 55-Gallon Reactor Vessel

Total reactant volume approximately 142 liters or 37.5 gallons.

Expected product yield approximately 12.5 kgs or 27.6 lbs.

1. **Formulate Reactant Solutions A and B as follows:**

   Reactant Solution A

   Reactant Quantities

Cinnamaldehyde	12.5 liters (13.2 kgs or 100 moles)
Methanol	12.5 liters

   Formulation Procedure

   Add 12.5 liters of cinnamaldehyde (ρ = 1.05 gms/cc) to 12.5 liters of methanol. Agitate to achieve a uniform solution.

   Reactant Solution B

   Reactant Quantities

Methanol	100 liters
Potassium hydroxide	4.5 kgs
Indene	17.5 liters

   Formulation Procedure

   Add 4.5 kgs of KOH (preferably flake to aid in dissolution) to 100 liters of methanol. Stir to achieve a uniform solution. Add indene (addition rate need not be controlled but temperature of KOH-methanol solution should be no higher than 35° C) and stir to achieve a uniform solution.

2. **Reaction Procedure**

   Add reactant Solution A to reactant Solution B at a controlled rate (suggest addition rate of 6 liters/hour or 100 cc/min). Solution B should be well agitated during the addition

and for 30 minutes after the addition is complete. The temperature of the methanol-KOH-indene solution should be within the range 25 - 35° C during the addition. The reactor need not be protected from air or moisture during the reaction. Cooling coils carrying tap water will allow the temperature to be controlled in this range.

3. **Work-Up Procedure**

At the end of the reaction period, the insoluble precipitate that forms should be collected by filtration, pulled free of reactant solution (but not dry), and washed with fresh methanol two or three times by flooding the filter cake and allowing liquid to flow through before a fresh wash liquid is added. (Necessity for additional purification may require an intermediate wash of the filter cake, or a slurry of the filter cake, in water, water-methanol, or methanol-acetic acid mixtures.) Product may be allowed to dry in air at ambient temperature (or in ovens at 60° C or less).

4. **Product Description**

Product will be orange in color and will melt over range from 172 to 190° C (theoretical, ~ 190° C). Yields are 50 - 60 percent of theoretical (calculations based on cinnamaldehyde).

5. **Analytical Procedures**

Analytical procedures used to certify the product were: (1) gel permeation chromatography (GPC), which shows major organic impurity as a secondary band, and (2) X-ray fluorescence for the potassium content. (Typical products are > 95 percent cinnamylideneindene.)

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