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MASTER

MATERIALS MEMORANDUM

To: L. A. Shurley

18 October 1971
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From: L. M. Swope

Subject: Results of Binder Screening Tests and Selection of Two Binder Compositions

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Reference:
(a) Materials Priority and Maturity Status Report, Para. 2.2, M-6 Graphite Composite - Nozzle Extension, dated 15 September 1971
(b) The Fabrication and Properties of the Fibrous Reinforced Graphite Composite 101, Report RN-S-0549, dated March 1970
(c) Development Specification ANS-90293 Nozzle Extension Assembly, Fabrication Feasibility

Enclosure: (1) Binder Selection Criteria

1. The purpose of this memorandum is to document the results of the binder development screening tests and to identify the criteria used to select two binder systems for further statistical property tests.

2. Screening tests were conducted on 26 binder compositions that were evaluated under Paragraph 2.2 of the M-6 Plan (Reference (a)). A supplementary small effort was also initiated at the request of Project 143 to preliminary examine the feasibility of using the gaseous chemical vapor deposition process (C.V.D.) for densification in lieu of the liquidus process as used for AGCarb-101. Since this effort was not included in the M-6 Plan, very little expenditure of funds could be committed for this effort. Three plates were fabricated using two methods for C.V.D. processing; two plates were densified at the Y-12 Plant, Oak Ridge, Tennessee using the gas pulse technique, and one plate was densified at Poly Carbon Company, North Hollywood, California, using the thermal gradient method. The results of property tests on these plates will be presented in a subsequent paragraph along with the property data on the 26 binder compositions.

3. In the selection of a binder composition, consideration must be given not only to high strength properties imparted to the composite but to such factors as costs, long term availability, compositional uniformity, re-use

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capability, handling characteristics, and susceptibility to radiation damage. In order to be able to more fully understand these criteria, a discussion of each of these factors is presented in Enclosure (1).

4. The impregnation conditions used for all these binder compositions are those set forth in Paragraph 3.6.1 of Reference (c). These conditions were selected to enable the impregnation process to be accomplished in the 120-inch autoclave since dual use of the autoclave was in the original proposal to NASA regarding ANSC manufacturing equipment capabilities.

5. Table I is a compilation of the average property data obtained on all of the 26 binder compositions - plus the results obtained from the three C.V.D. plates. Also included with this data is the results obtained from a plate that was densified at Union Carbide using their proprietary Code 88 treatment. This impregnant is used for the manufacture of AGCarb-101. For each composition testing consisted of 3 each interlaminar shear, 3 each block tensile and one modulus of elasticity in the warp fiber direction. One additional re-test was performed for each set of data whenever one of the three data points revealed a significantly lower value. A review of the property data shows the following range in properties obtained for the 26 binder compositions, the C.V.D. panels, and the AGCarb-101 panel:

		Interlaminar Shear (psi)	Block Tensile (psi)	Modulus (10^6 psi)
A.	26 Compositions	932-1372	332-740	2.45-3.25
B.	C.V.D. Y-12	1122-1130	535-678	2.12-2.40
C.	C.V.D. Poly Carbon	1054	436	2.62
D.	AGCarb-101	1367	468	2.35

The highest average interlaminar shear strength, 1372 psi was obtained from the composition (P/N 1008) 15V pitch* + indene** (72:25 mixture ratio by weight). The highest average block tensile strength was obtained with the composition (P/N 1097) which exhibited a strength of 740 psi. This composition is a 50:50 mixture of 15V pitch + Fapreg P-3.*** All of the C.V.D. panels

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* Coal tar pitch manufactured by Allied Chemical Co.

** Organic Solvent - $C_6 H_4 CH_2 : CH$

*** Thermo setting resin manufactured by Quaker Oats.

were significantly lower in interlaminar shear strength. One of the panels produced at Y-12 with a density of 1.39 did exhibit a block tensile strength typical of AGCarb. The block tensile strength of the AGCarb-101 was significantly lower than 638 psi strength previously obtained, (Reference (b)) for this material. The modulus of elasticity values fell within the ranges generally found for graphitized fibrous graphite compositions.

6. A computerized correlation analysis was conducted on all the test data to determine if any relationships exist between all six combinations of the four properties measured. i.e., block tensile strength, modulus of elasticity, interlaminar shear strength, and density. It was intended that if relationships were found to exist, further developmental efforts could be directed toward those variables which related to improving overall strength properties.

The lack of correlation (all correlation coefficients were below .56*) indicated that intrinsic characteristics for each binder composition was affecting each of the measured properties differently. Therefore, the basis for selecting a binder system could not be made on a statistical basis. Each binder composition had to be evaluated relative to its effects on the primary properties measured, - interlaminar shear, modulus, block tensile and density.

7. The procedure for selecting the two best binder compositions for the property characterization tests required per Paragraph 2.3 (Reference (a)), involved devising a numerical rating system whereby each composition could be rated on an individual basis. This rating system is defined in Table II which also presents the results of the ratings for each composition. The system was based upon the maximum achievable score of 100 points. Sixty percent of the rating is based upon strength properties, and the balance of 40% is divided at 10% for each of the other four rating criteria, i.e., long term availability, estimated use life, processability, and costs.

The composition, 15V pitch + Indene with a mixture ratio of 3:1 by weight, (P/N 1008) achieved the highest rating of 86 points and therefore has been selected as the first of the two candidate compositions. This composition was selected for the densification of the six Intremold III cylinders.

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* Above .75 considered significant correlation for this type material.

The second composition selected, 15V pitch + P-3 with a mixture ratio of 1:1 by weight (P/N 1097) had the next highest numerical rating of 82 points. Intelligence gained from vendors indicates this mixture approximates the Code 88 pitch system used by Union Carbide for the densification of AGCarb-101.

These two binder compositions will now be used for the series of property characterization tests scheduled in the M-6 Plan.

8. Y-12 personnel were contacted in reference to the selection of these two binder compositions. John Napier, Y-12, indicated the only problem he observed with the 15V pitch is the increasing re-melt temperature with re-use. He stated the 15V + P-3 provides a glassy carbon structure which is less desirable when thermal shock is a problem.

He told of a cooperative program with Quaker Oats Company, Chicago, Illinois to develop binders around Ashland Oil petroleum pitches for fabricating NERVA fuel elements. These pitches are considered to be the best from the standpoint of long term availability and batch-to-batch controllability. Napier reviewed the systems they have investigated to date and recommended a Quaker Oats experimental Grade QX-309-1. This binder has been found to have the same structure as the 15V pitch and is graphitizable, and hence would provide a low modulus matrix.

From a processing viewpoint, these pitch systems are highly desirable since they are liquidus at room temperature. Very little heating would be required to reduce the viscosity to the required 50 centipoise level.

9. Quaker Oats has been contacted regarding the availability of a 10 gallon sample of the QX-309-1 for evaluation. This grade plus two other grades, QX-297-1 and QX-298-1 will be shipped to ANSC very shortly. In addition, their development personnel are planning a visitation to ANSC early in November to discuss our requirements in more detail.

10. In regard to the C.V.D. process, further evaluation of only the gas-pulse technique used by the Y-12 plant are warranted. Additional impregnation studies are required to determine if the process is capable of penetrating the thick flange sections that would exist with either the Intremold III material or a laminate layup such as a rosette or shingle lap layup. An engineering evaluation should also be made of the process in terms of feasibility of scaleup relative cost trade-offs in comparison to a liquidus system as well as the capability of the large induction furnace to meet the process requirements.

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Materials Section

Enclosure (1)
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BINDER SELECTION CRITERIA

A. Long Term Availability

Carbonaceous pitches are by-products of either coal tar or heavy refinery oil distillation. The properties of these pitches are highly dependent upon their precursor raw material. Product variability inherently occurs when a change occurs in the source for the raw material. This change is generally necessitated by a depletion of the natural occurring supply. This problem has plagued the graphite industry for years. It is imperative that the pitch system selected be available for the length of the production schedule for the NERVA engine. An alternate solution to this is the stockpiling of a production lot of pitch since this product has an infinite storage life.

B. Compositional Uniformity

The problem of compositional uniformity from batch-to-batch is closely related to the variability in raw material as discussed above. Since compositional control closely affects process controls and the resultant properties of the composite, it is vital that rigid procurement specifications be established and be adhered to by the supplier. This in turn necessitates the selection of a pitch manufacturer with the resources and reputation for a high quality product.

C. Re-Use Capability

A significant consideration is the ability to be able to re-melt and re-use the binder for a number of impregnation cycles. A characteristic of most pitches is the tendency for the melting point to increase as recycling occurs. This occurs as a result of the volatilization of low molecular weight hydrocarbons. Adjustments in melt temperatures can be affected by the addition of solvents which is turn affect process conditions and composite strength properties.

Re-use capability can become seriously limited by the use of additives to cause thermosetting of the thermoplastic pitch. Thermosetting of the binder after impregnation is desirable as it prevents the pitch from remelting and exuding from the structure during the carbonization cycle. The use of thermosetting additives generally requires close temperature control during impregnation to prevent the pitch from thermosetting during impregnation. Also many of these compounds have a short term pot life which requires a fresh batch of binder for each impregnation cycle.

D. Handling Characteristics

There are a number of factors to be considered involving the handling characteristics of the binder. One factor is the explosive nature of the fumes being evolved during heating and impregnation. This hazard is generally the result of the type of solvent used to reduce the viscosity. Benzene for example, is a particularly hazardous solvent for pitch because of its low flash point. Also, vaporization or boil-off is a problem during impregnation with solvents and thermosetting liquids such as furfural alcohol. This occurs when the part is subjected to a high vacuum prior to submerging in the pitch.

E. Costs

Costs become significant when viewed in terms of the large quantity of binder required for impregnating the Nozzle Extension. Depending upon the design of the impregnation equipment, a minimum quantity of binder needed has been estimated to be 20,000 lb. Costly binders such as the Y-12 isotruxene, which in production would cost $9.00 per lb, practically eliminates these materials from serious consideration. Costs become of particular importance if the binder has limited re-use capability.

F. Radiation Damage

True graphitic binders such as a straight pitch system, are least susceptable to radiation damage as compared to compositions such as furfural alcohol and phenolic resins which exhibit glassy carbon structures. The effect of damage under the fluence levels anticipated for the nozzle extension on composites with thermosetting additives to the pitch remains to be determined.

TABLE I

RESULTS OF PROPERTY SCREENING TESTS

COMPOSITION	MIXTURE RATIO (BY WT)	P/N	DENSITY g/cm^3	INTERLAMINAR SHEAR * PSI	BLOCK TENSILE * PSI	MODULUS OF ELASTICITY 10^6 PSI
A. 26 Compositions						
170 + P-3	3:1	1005	1.33	993	332	2.80
15V + P-3	3:1	1006	1.38	1012	464	2.81
170 + IND	3:1	1007	1.41	1075	449	2.98
15V + IND	3:1	1008	1.48	1372	668	3.25
P-3 (no catalyst)		1009	1.42	1079	554	2.81
F.A (2% oxalic acid)		1010	1.41	1144	582	2.76
15V + F.A.(2% oxalic acid)	3:1	1027	1.42	1296	613	2.49
15V + F.A.(2% oxalic acid)	1:1	1028	1.37	1072	638	2.52
15V + ITX + IND	4:2:3	1029	1.44	1209	530	2.64
15V + DEN 438 + IND	1:1:1	1030	1.44	1322	567	2.73
15V + ITX + IND	1:1:1	1031	1.48	1283	562	2.70
15V + USP-39 + IND	2:1:1	1032	1.39	1170	533	2.55
15V + USP-39 + IND	1:1:1	1033	1.42	1323	575	2.71
15V + EC-260 + BEN	2:1:1	1034	1.41	1329	639	2.92
DEN 438		1035	1.39	983	555	2.94
USP-39		1036	1.40	1292	642	2.85
CA 2223		1037	1.38	1273	648	2.92
15V + VAR + IND	2:2:1	1054	1.41	1178	615	2.90
15V + CA 2223	1:1	1055	1.41	1320	517	2.77
(Pretreat F.A.) 15V + IND	3:1	1081	1.48	932	555	2.76
524 + P-3	3:1	1083	1.43	1251	646	2.66
(Pretreat F.A.) 15V + IND	3:1	1084	1.47	1198	652	2.90
EC-260		1086	1.32	1083	454	2.48
15V + P-3	1:1	1097	1.47	1265	740	2.81
140		1111	1.39	1082	488	2.45
170		1112	1.40	1113	450	2.49

TABLE I (Continued)

COMPOSITION	MIXTURE RATIO (BY WT)	P/N	DENSITY g/cm^3	INTERLAMINAR SHEAR * PSI	BLOCK TENSILE * PSI	MODULUS OF ELASTICITY 10^6 PSI
B. Chemical Vapor Deposition						
Poly Carbon - Thermal Grad.		1075	1.31	1054	436	2.62
Y-12 Gas Pulse Tech.		1088	1.39	1130	678	2.40
		1089	1.33	1122	535	2.12
C. AGCarb-101		1076	1.41	1367	468	2.35

* Average of a Minimum of 3 Tests.

LEGEND

Grade 170 = Ashland Oil Grade 170 Petroleum Pitch
Grade 140 = Ashland Oil Grade 140 Petroleum Pitch
Fapreg P-3 = Quaker Oats Furfural Alcohol Monomer System
15V = Allied Chemical Grade 15V Coal Tar Pitch
F.A. = Quaker Oats Furfural Alcohol
IND = Indene-Organic Solvent
ITX = Y-12 Plant Isotruxene

DEN 438 = Dow Corning Epoxy Novalac
USP-39 = U.S. Polymeric Prepreg Resin
BEN = Benzene
CA 2223 = Ferro Prepreg Resin
VAR = Varcum Reichold Chemical
524 = Allied Chemical Grade 524 Coal Tar Pitch
EC-260 = Evercoat Chemical Prepreg Resin

TABLE II

RATING SYSTEM FOR SELECTING TWO CANDIDATE BINDER COMPOSITIONS

COMPOSITION	MIXTURE RATIO (BY WT)	P/N	STRENGTH$^{(1)}$ BLOCK TEN,	INTER SHEAR	LONG TERM$^{(2)}$ AVAILABILITY	ESTIMATED$^{(3)}$ USE LIFE	PROCESS$^{(4)}$ ABILITY	$^{(5)}$ COSTS	TOTAL NUMERICAL RATING	TWO HIGHEST CANDIDATES
170 + P-3	3:1	1005	10	10	9	4	7	9	49	
15V + P-3	3:1	1006	15	15	8	4	7	9	58	
170 + IND	3:1	1007	15	15	8	8	7	5	58	
15V + IND	3:1	1008	25	30	10	8	8	5	86	1
P-3 (no catalyst)		1009	20	15	9	4	7	6	61	
F.A. (2% oxalic acid)		1010	20	20	10	1	2	8	61	
15V + F.A.(2% oxalic acid)	3:1	1027	25	25	10	3	3	9	75	
15V + F.A.(2% oxalic acid)	1:1	1028	25	15	10	3	4	9	66	
15V + ITX + IND	4:2:3	1029	20	25	1	3	4	1	54	
15V + DEN438 + IND	1:1:1	1030	20	30	8	3	4	3	68	
15V + ITX + IND	1:1:1	1031	20	25	1	3	4	2	55	
15V + USP-39 + IND	2:1:1	1032	20	20	9	2	4	2	57	
15V + USP-39 + IND	1:1:1	1033	20	30	9	2	4	1	66	
15V + EC-260 + BEN	2:1:1	1034	25	30	4	2	4	0	65	
DEN 438		1035	20	10	8	1	4	4	47	
USP-39		1036	25	25	9	2	4	2	67	
CA 2223		1037	25	25	9	2	4	5	70	
15V + VAR + IND	2:2:1	1054	25	20	9	3	4	2	63	
15V + CA 2223	1:1	1055	20	30	9	2	4	7	72	
(Pretreat F.A.) 15V + IND	3:1	1081	20	10	9	8	8	5	60	
524 + P-3	3:1	1083	25	25	9	4	7	9	79	
(Pretreat F.A.) 15V + IND	3:1	1084	25	20	10	8	8	5	76	
EC-260		1086	15	15	4	2	4	0	40	
15V + P-3	1:1	1097	30	25	8	4	7	8	82	2
140		1111	15	15	10	8	9	10	67	
170		1112	15	20	10	8	8	10	71	

Grade 170 = Ashland Oil Grade 170 Petroleum Pitch
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TABLE II (Continued)

RATING SYSTEM

Maximum Rating = 100 Points
60% Total Rating Based upon Strength Properties
10% Long Term Availability
10% Use Life
10% Processability
10% Costs

(1) Strength	RATING, POINTS 30	25	20	15	10
Inter. Laminar, psi	>1300	>1200	> 1100	> 1000	> 900
Block Tensile, psi	> 700	> 600	> 500	> 400	> 300

(2) Long Term Availability

Points	
8 - 10	Commercial AVailability Foreseen for Next 10 Years
5 - 7	Changes in Availability Could Occur Over Next 10 Years
2 - 4	Limited Production
0 - 1	R & D Status

(3) Estimated Use Life

Points	
6 - 10	6 Cycles or More
4 - 5	4 - 5 Cycles
2 - 3	2 - 3 Cycles
0 - 1	1 Cycle

(4) Processability

Points	
8 - 10	Straight Pitch - No Solvent
5 - 7	Pitch or Resin with Solvent - No Thermoset Additive
2 - 4	Pitch or Resin with Solvent and Thermoset Additive
0 - 1	Extreme Boil-off Under Vacuum

(5) Costs

Points	Price/Gallon $
6 - 10	Up to 5.00
3 - 5	5 - 20
2	20 - 40
0 - 1	> 40