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TELEX 848-432

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Final Report

NASA CONTRACT # NAS8-32317

MOLDABLE CORK ABLATION MATERIAL

INTRODUCTION

At the request of H. McMahan Walker (EH43) of the National Aeronautics and Space Administration, Marshall Flight Center, Dodge Cork Company, Inc. undertook to establish the feasibility of producing a moldable cork ablative insulation material. While cork has been used as an ablative material for a number of years, it's usage was limited not only by it's thermal characteristics, but also by it's inability to be draped over complex shapes. It was Mr. Walker's hope that Dodge could develop a thermal insulation material that could be formed easily over the various complex configurations that might be necessary on a space vehicle. His idea derived from his experience with phenolic-fiber "pre-pregs", where a phenolic resin acts as a thermoplastic in its "B" stage then as a thermoset in its final one. It was Dodge's assignment to examine the practicality of his "cork pre-preg" concept. Our ideal solution was a cork sheet that had enough inherent integrity to be handled, enough flexibility to allow for molding over complex shape and sufficient final properties to justify its use as a thermal insulating material. In addition we hoped that the sheet could be molded and cured in place, to allow for a sample and elegant solution to the problem of insulating reusable systems. With the "pre-preg" concept in mind, Dodge does come a long way in establishing the viability of this idea and hopefully a long way toward producing a useful material for many ablative applications for our space programs.

BACKGROUND - Why Cork?

Being a readily available natural product, cork is often bypassed by science and industry in favor of our modern synthetic "replacements". Cork, the bark of the cork oak tree (*Quercus suber*), is nature's foam; a foam with a unique combination of properties yet to be duplicated by man. A cubic inch of natural cork consists of approximately 200,000,000 minute cells, each completely closed and filled with air. These cells average about 1/1,000 of an inch in diameter and each is separated from the other by a thin, but remarkably strong resinous membrane. Slightly more than 50% of the volume of a piece of cork is accounted for by the captive air within the cells. Even more remarkably nature has endowed cork with a "perfect" internal structure. Lord Kelvin established the fact that it takes 14-sided bodies or areas (a tetrakaidechedron) to solve the problem of dividing up space without interstices into a uniform body of minimum surface dimensions. Cork cells are 14 sided. Thus, cork is completely cellular with no empty space between the cells.

The unique structure of cork gives rise to unique properties. Cork has a low density, is highly compressible, extremely resilient, has a very high resistance to moisture or liquid penetration (no interstices), a high coefficient of friction, low thermal conductivity, an ability to absorb vibration and excellent stability. This unique combination of properties has made cork and cork products extremely versatile over the years. Records of the use of cork date back to the times of the Ancient Greeks who used it for shoe soles and to seal liquid storage vessels. Its present use runs the gamut from sophisticated applications such as ablative material to more mundane applications like bulletin boards, machine vibration mountings, all types of gaskets, floor underlays, shoe soles, floor and wall tiles, and, of course, wine bottle closures.

The properties which make cork a potential ablative insulating material are, of course, its low density, low thermal conductivity, inherent stability, and the way in which it burns. The raw cork used in our formulations, known as select cork, has a density of 3 - 3.5 lbs. per cubic foot. This obviously is advantageous where dealing with payloads of space vehicles.

Natural cork has a K factor of 0.25 BTU/hr./ft.^{2}. The low thermal conductivity being caused by the trapped air structure of cork. Given the low density and the large number of cells in a cubic inch of cork a little bit of cork goes a long way as an insulator. Compounds with densities as high as 35 pcf. and containing 25 - 30% cork by weight will still have a K factor of as low as 0.4.

The burning characteristics of cork are naturally related to its low thermal conductivity. Cork, as a natural wood, burns on ignition, but with its foam-like structure the heat of combustion simply is not transferred very deeply into the material. Thus, the formation of successive layers of char is dependent upon a constant supply of heat. As soon as heat is removed the cork will self-extinguish. Tests done by the United Kingdom Atomic Energy Authority in 1967 show this property clearly. A 8" diameter by 10" long cork container with a 4" diameter core containing a 10 ml. vial of water was subjected to a heat of 800°C.for 30 mins. By use of thermocouples the temperature of the water was measured for the duration of the test. At no time during the test did the temperature of the water exceed its boiling point (100°C.). The cork charred only to an approximate depth of only 1 inch, thus illustrating the ability of cork to carry incident heat away from a potentially heat absorbing area.

Thus, to return to our initial question, to understand why cork, a naturally occurring substance in use for over 2000 years, should be incorporated into the most technologically advanced systems presently considered by man, one has only to look at cork's unique and "perfect" structure, a structure that yields a combination of properties that to a great degree coincide with those of the ideal ablative insulation material.

OBJECTIVES

The objectives as understood through verbal contacts between NASA and Dodge, and as outlined in the contract covered three general areas of experimentation.

Area 1. Was the concept of cork "pre-preg" possible in any way, shape, or form? Dodge sought to examine various types of resins in various combinations with cork and plasticizers to ascertain if any of these combinations could yield a handable sheet that could be successfully molded over complex shapes. In addition, General Electric, our subcontractor, was to work with us to delineate which type of molding technique, if any, could best be used with a cork pre-preg.

Area 2. How would the moldable cork sheet perform and stack up against existing cork ablation material? As part of the contract Dodge would attempt to produce 300 lbs. of moldable cork sheets which would be tested against presently qualified cork ablation material. Dodge and GE were to test some specific properties, namely, density, tensile strength, tensile elongation, thermal conductivity, compression set, and specific heat against the present qualifying standards set by the Armstrong 2755 material. It was assumed by all parties that NASA would conduct other tests itself to evaluate other relevant properties, especially radiant and convective heat of ablation.

Area 3. <u>What are the maximum properties that could be obtained by cork "pre-pregs" and what production difficulties would be presented to Dodge in the manufacture of this type of material</u>? These really were two separate but closely related areas. Dodge tried to suit the formulations to approximate present production methods, but always with an eye toward maximizing the end product. The degree to which quality of a product and efficiency of processing are compatible had to be ascertained. In addition cost, quality, storage life, and transportation methods had to be considered. Essentially, this area of experimentation dealt with practical problems involved in bringing a viable lab concept into viable production items.

This report, then, is a detailing of the experimentation undertaken in cork of these areas and an explanation of the results obtained.

EXPERIMENTATION

Area 1: Formulation and Testing og Moldable Cork Sheets

1.1 Material ABL-10

1-1.1 As a base line material Dodge started with its version of the present (P-50) type ablative material, simply modified with a "longer flow" resin. Our concept was to make a flexible composition at 15 pcf. density with a nominal thickness of .250" which was to be compressed 50% to yield a finished sheet of 30 pcf. with a thickness of .125". We felt that a 15 pcf. sheet would be more drapable than a 30 pcf. sheet. Mats were compounded and split to .250" and denoted as ABL-10. This material was submitted to GE to provide insight into future avenues of exploration. Dodge suggested the following molding cycle as a starting point to densify the sheets:

145 psi.
310°F.
15 - 20 min.

This cycle implied the necessity of autoclave processing to produce shaped parts. To zero on molding parameters flat sheets were press molded. In addition, to assess formability of this type of sheet, material was vacuum bag molded over an 18" diameter machined aluminum hemisphere.

1-1.2 Evaluation: As indicated by Table 1 all sheets but one fell within the 14-15 pcf. density range. Table 2 briefly lists the molding cycles attempted and the results.

TABLE 1

ABL NO.	LOT NO.	SHEET NO.	AVERAGE THICKNESS INCHES	WEIGHT GRAMS	DENSITY PCF
10	1	1	.259	143	14.7
		2A	.262	76	15.6
		2B	.257	79	15.6
		3	.269	149	14.9
		4	.264	146	14.8
		5	.264	144	14.6
		6	.265	143	14.4
		7	.262	139	14.1
		8	.263	140	14.1
		9	.263	140	14.1
		10	.264	141	14.3
		11A	.256	68	14.2
		11B	.260	68	14.3
		12	.259	141	14.5
		13A	.257	68	14.3
		13B	.259	67	14.1
11	1	1A	.257	68	14.1
		1B	.257	67	14.0
		2	.230	122	14.1
		3	.246	130	14.0
		4	.472	259	14.6
		5	.512	299	15.6
		6	.487	261	14.2
	2	7	.248	196	20.9
		8	.247	195	21.0
		9	.250	200	21.1
		10	.482	428	23.6
		11	.489	409	22.3
		12	.374	227	21.3
		13A	.367	147	21.2
13	1	14	.382	281	19.6
		15	.072	58	21.2
		16	.384	292	20.1
		17	.387	295	20.2
		18	.480	388	21.2

TABLE 1 (CONT'D)

ABL NO.	LOT NO.	SHEET NO.	AVERAGE THICKNESS INCHES	WEIGHT GRAMS	DENSITY PCF
15	1	A	.257	233	24.4
		B	.274	264	25.9
		C	.283	271	25.8
		D	.288	283	26.4
		E	.289	289	26.9
		F	.294	285	26.1
	2	A	.083	101	32.7
		B	.237	242	27.5
		C	.252	247	26.4
		D	.259	248	25.8
		E	.258	255	26.6
		F	.262	261	26.8
		G	.263	264	27.0
		H	.264	271	27.6
		I	.263	264	27.0
		J	.265	264	26.8
		K	.262	261	26.8
		L	.263	260	26.6
		M	.263	257	26.3
		N	.263	252	25.8
		O	.259	247	25.6
		P	.308	315	27.5
	3	A	.138	146	28.5
		B	.283	312	29.7
		C	.254	254	26.9
		D	.256	252	26.5
		E	.261	254	26.2
		F	.263	267	27.3
		G	.264	261	26.6
		H	.262	268	27.5
		I	.255	259	27.3
	PROD	1	.265	1343	27.6
		2	.260	1309	28.7

TABLE 2

ABL 10 LOT 1 MOLDING

SHEET NO.	CYCLE	RESULTS
1	150 ± 10 psi 310°F for 15 minutes	Thickness = .080 Density = 50 PCF
3	150 ± 10 psi (cold press) RT to 310°F in 1 hour 310°F for 15 minutes	Thickness = .070 Density = 55 PCF
4	Vacuum Bag (15 psi) RT to 310°F in 1-1/2 hours 310°F for 15 minutes over shaped fixture	Thickness = .26" Density = 15 PCF Cracks formed at sharp radius
5	Preheat sheet at 200°F for 1 hour. Apply vacuum and raise temp. to 310°F in 15 minutes and hold for 15 minutes.	Same as #4 except cracks at sharp radius less than #4
6	Sheet soaked in 180°F water for 1-1/2 hours (Wt. increased from 143 gms to 389 gms). Vacuum bag: RT to 200°F in 30 minutes. 200°F for 15 minutes. 200-300°F in 15 minutes. 300°F for 15 minutes.	Very pliable after water soak. Cured weight = 152 gms. Thickness = .27" Density = about 15 PCF Some cracking
7	100 ± 20 psi, 310°F for 15 minutes	Thickness = .085" Density = 45 PCF
8	70 ± 10 psi, 310°F for 15 minutes	Thickness = .09" Density = 40 PCF
9	50 psi at 310°F for 15 minutes	Density = 33 PCF
2A	50 psi at 310°F for 20 minutes	Thickness = .107" Density = 37.2 PCF
2B	Immersed in 120°F water for 2 hours. 35 psi. RT to 310°F. Hold at 310°F for 20 minutes	Thickness = .117" Density = 29.8 PCF

TABLE 2 (CONT'D)

SHEET NO.	CYCLE	RESULTS
11A	40 psi at 310°F for 20 minutes	Thickness = .099" Density = 35.7 PCF
11B	35 psi at 310°F for 20 minutes	Thickness = .112" Density = 31.4 PCF
13A	Immersed in 120°F water for 15 minutes. 35 psi at 310°F for 20 minutes	Thickness = .104" Density = 31.6 PCF
13B	24 hours at 95% RH	6" wide strip - could not form over 3" radius hemisphere; cracked over 4.5" radius hemisphere; OK over 9" radius

1-1.3 Discussion of Results: As can be seen in Table 2 various cycles were attempted as well various preparations for molding, such as, preheating and pre-soaking in water. The data indicated that a pressure of 35 psi. would mold the ABL-10 composition to about a 30 pcf. density. These conditions, for shaped parts, could be accomplished in an autoclave. The ABL-10 material could be moderately shaped, but even at atmospheric pressure and when wet, the tendency to crack was pronounced. A far more flexible formulation was indicated. Thus, it was decided that Dodge should reformulate to obtain the maximum flexibility possible with this type of compound.

1.2 Material ABL-11, ABL-12, ABL-13

1-2.1 Each of the formulas, ABL-11, ABL-12, and ABL-13 were variations of the ABL-10 system to increase flexibility. In ABL-11, two separate variables were changed. First the amount of plasticizer was increased, then, in addition to increasing the plasticizer, the mat was molded at a 22.5 pcf. density. It was hoped the higher density would help prevent cracking in molding and reduce the amount of pressure necessary to obtain a 30±2 pcf. density. (At this point we should note that the 30±2 pcf. density was chosen based on the Armstrong 2755 standard. We, at Dodge, not having the equipment to test heat of ablation, assumed

Armstrong chose this density via testing of various densities and considered this to be the maximum.). In ABL-12, the amount of resin in the system was increased with the hope of increasing the inherent strength of the compound, and thus allowing it to be molded without cracking. In ABL-13, the amount of cork was reduced and both the resin and plasticizers increased, hoping to incorporate any improvement noted in ABL-11 or ABL-12.

i-2.2 Dodge tested these formulations for flexibility only, the results of which we listed on Table 3-A. Samples of ABL-11 and ABL-13 were sent to GE to test for formability. Highlights of GE's tests make up Table 3-B.

Table 3-A

Flexibility is defined as the ability of a piece to be bent around X times the sheet thickness.

X = flexibility

ABL No.	Lot No.	Variable	Flexibility
10	1	Base line	6.9
11	1	Increased plasticizer	6.1
	2	Increased plasticizer, increased density	5.3
12	1	Increased resin	5.7
13	1	Increased resin, increased plasticizer, increased density	5.3
	2	Increased resin, increased plasticizer, decreased cure time	4.0

TABLE 3 - B

ABL NO.	LOT NO.	SHEET NO.	PROCEDURE	RESULTS
11	1	1A (6"x12")	No conditioning. Press molded at 35 psi at 310°F for 20 minutes	Thickness = .104" Density = 33.1 PCF
		1B (6"x12")	As above but 30 psi	Thickness = .107" Density = 32 PCF
		2	20 hours at 100% RH. Molded at 14 psi, RT to 310°F, then 20 minutes at 310°F	Thickness = .131" Density = 23.6 PCF
		3	17 hours at 100% RH. Molded at 28 psi, RT to 310°F, then 20 minutes at 310°F	Thickness = .105" Density = 31.6 PCF
11	2	8	18 hours at 98% RH. Molded like sheet 3 above	Thickness = .151" Density = 31 PCF (10% pickup in wt. from conditioning). Cracks propagated from corners after molding.
		12	15 minutes in 120°F water (15.5% by weight water pickup). A 11-3/4" circle cut from sheet. Vacuum formed over 18" diameter and 9" diameter hemisphere	Formed over 18" diameter but folded and crumpled over the 9" diameter hemisphere
11	2	12	Pieces of this sheet (as rec'd) soaked in acetone, methyl alcohol and toluene to determine affect on flexibility	No changes observed. No softening, swelling or resin extraction

1-2.3 <u>Discussion of Results</u>: As Table 3-A indicates there was some increase in flexibility in each formula change. However, Table 3-B shows the difficulty in molding hemispheric shapes of ABL-11 Lot 1 and 2 by vacuum forming techniques. Sheets from ABL-13 Lot 1 were similarly handled with similar results. It became clear that the resin in the sheets simply was too far advanced; no flow was observed during cure and no resin could be extracted by several solvents. At this point, it seemed fruitless to pursue the project along these lines. We had made a fundamental error in looking for increased flexibility rather than increased "flowability". Even if the ideal flexibility were obtained the sheet would act much like a sheet of paper. It would always wrinkle at the maximum circumference since the particles are too tightly bound together to move relative to each other. The key to solving the moldability problem was then to find a resin that would bind the cork particles sufficiently together to allow for handling, yet still allow enough flow so that the cork particles could move to some degree within the sheet. No combination of the resin used in ABL-10 - 13 would allow for this type of internal flowability.

1-3 ABL-14 and ABL-15

1-3.1 Based on the concept of increasing flowability two alternative systems were selected. The first was a "castable" resin system. This is a very high viscosity two-part phenolic system. It is commonly used in making phenolic die castings. When the two parts are heated together a relatively flowable liquid is formed, however when the mixture is cooled, the resin forms a hard block. This process could be repeated quite a few times before the resin reached final cure. The idea was to heat the two part resin just enough to allow complete mixing with cork, then mold the mixture into block form, which would then be cooled sufficiently to form a solid block. The block would be split into sheets. Subsequent heating would cause the resin to flow again, thus allowing the finished sheet to be molded on the hemisphere. The second system was to use a resin designed to have a very long "B" stage. This resin would be mixed with cork, molded into blocks, the state of cure regulated so as to give sufficient initial tensile strength to be molded, yet still retain the necessary degree of internal flow to allow forming. In both cures a departure was made from standard ablative cork formulation by increasing the cork-resin ratio to allow greater internal flow. It was hoped that reduction of cork loading would have a minimal effect on the significant properties due to the low specific gravity of cork. In addition, the concept of compressing 15 pcf. cork sheets to 30 pcf. was abandoned in that molding in place by vacuum forming was the most desirable molding technique from NASA's standpoint.

1-3.2 Evaluation: A rather simple test was established at Dodge to roughly check the moldability of the experimental formulations. A half of a soft ball (a 4¼" diameter hemisphere) was used as a form with a solid retaining ring used to force the sheets to conform to the hemisphere. Rough formulations based on Dodge's previous experience with cork were tried out with both resin systems. The castable resin was heated then mixed in a hot (175°) mixer with cork. A block was molded at 30 pcf. density, then immediately cooled to 40°F. in the mold. After 24 hrs. the mold was broken and the block split. There was sufficient integrity for ¼" sheets to be successfully split from the block. The long "B" stage resin was mixed and molded by normal production methods. These mats were molded to a 30 pcf. density. Various cork-resin ratios and cure cycles were tried. Both systems were tried on the 4½" hemisphere. The results are listed in Table 4.

Table 4

ABL NO.	Lot No.	Procedure	Results
14	1	$\frac{1}{4}$" sheets heated to 150° by heat lamp, molded over $4\frac{1}{2}$" hemisphere by use of mechanical retaining ring	when heated for less than 5 min. material too stiff to mold. cracked when heated more than 5 min. integrity of piece broke down, became particulate mass. unable to mold with technique employed.
15	1	high resin content, sheet cut into 5-7/8" diameter. heated to approx. 150°F. with heat lamp, molded over hemisphere with retaining ring. baked at 100°F. for 6 hrs.	excess resin bled out of mold. material could be molded without cracking or folding. initial tensile approx. 100 psi. final density approx. 20 pcf.
	2	slightly lower resin content. same procedure as lot 1. baked at 100°C. for 8 hrs.	no resin bleeding. could be molded without cracking. initial tensile approx. 130 psi. final density approx. 28 pcf.
	3	same resin as lot 2. same molding. baked at 100°C. for 4 hrs.	some slight cracking when molded.

1-3.3 <u>Discussion of Results</u>: ABL-15 seemed to be exactly the combination we were looking for. It retained sufficient flow to allow molding. Consequently pieces were submitted to GE for conclusive proof by molding over the 9" hemisphere. Also GE would attempt to define the best molding technique. ABL-14 showed some promise, but it was questionable whether the sheet, once returned to its "mix" or particulate form could be reintegrated as part of the molding procedure. It might be possible to do so by some combination of techniques, but given the amount of money available the ABL-15 concept seemed the simpler of the two solutions.

1-3.4 <u>General Electric's Evaluation of ABL-15 Lots 1, 2, 3</u>: The ABL-15 formulation as received had promising resin flow characteristics and became soft and pliant when preheated to about 200°F. The densities of the sheets were in the upper twenties (pcf.) and did not need additional densification. Sheets from Lots 1, 2, and 3 were evaluated by three separate molding techniques; vacuum bag molding, molding ring forming, and vacuum bag molding with a calculated excess removed. The fixtures used were (#1) a 9" diameter machined aluminum hemisphere with small cylindrical section of the same diameter and (#2) a NASA part provided by Mr. Walker consisting of a domed shape with flanges. In addition, an aluminum molding ring was fabricated to assist in forming the ABL-15 on the 9" hemisphere. The ring was $1\frac{1}{2}$" high, $1\frac{1}{2}$" wide, $9\frac{1}{2}$" diameter at the base and shaped along its inside surface to the same contour as the hemisphere. Holes were drilled in the molding ring to line up with guide pins located in the base plate supporting the hemisphere. Table 1 lists the density of all the sheets in all the ABL-15 lots tested by GE. Table 5 outlines forming trials and pertinent results.

Table 5

9" Diameter Hemisphere

Vacuum Bag

Sheet I.D.	Density	Procedure	Results
1,A	24.4	10-7/8" diameter circle cut. sheet and hemisphere at ambient temp. 1 at. of vacuum applied	"crinkling" around lower $\frac{1}{4}$ of shape
1,B	25.9	10-7/8" diameter circle cut. sheet and hemisphere preheated to 200°F. 1 at. vacuum applied.	crinkling around lower $\frac{1}{4}$ of shape
1,C	25.8	10-7/8" diameter circle cut. sheet soaked 1 hr. in 120°F. water. hemisphere preheated.	crinkling around lower $\frac{1}{4}$ of shape
1,D	26.4	10-7/8" diameter circle cut. sheet heated to approx. 200°F. partial vacuum (about 10" mercury) applied. sheet manipulated by hand to try to smooth out "crinkles". then 1 at. vacuum applied.	sheet still crinkled. crinkles smaller, but more numerous.

Table 5 (Cont.)

Mold Ring Forming

Sheet I.D.	Density	Procedure	Results
2,E	26.6	sheet preheated at 200°F. for 5 min., formed over dome in single motion. cure: 300°F. for 30 min.	sheet split across top.
2,F	26.8	sheet cut into 10-7/8" diameter circle. preheated 200°F. for 5 min. mold preheated to 200°F. formed over dome in single motion. cure: 300°F. for 30 min.	sheet cracked at top
2,G	27.0	sheet cut into 10-7/8" diameter circle. preheated 200°F. for 5 min., mold preheated 200°F. formed in 2 motions (5min. between) cured: 300°F. for 30 min.	cracks at top of sheet
2,H	27.6	sheet cut into 10-7/8" diameter circle. preheated 200°F. for 5 min. mold at 200°F. formed in 4 successive motions (about 3 mins. bet. stages) then cured at 300°F. for 30 min.	OK
2,I	27.0	same as 2,H	OK

Table 5 (Cont.)

Vacuum Bag with Excess Removed

Sheet I.D.	Density	Procedure	Results
3,E	26.2	cut 11-7/8"circle (full size). soak for 1 hr. in 70°F. tap water. form in single motion over 200°F. form. cure: 200°F. for 60 min., 300°F. for 30 min.	OK across top. some cracks where retaining ring compressed material.
3		cut V shaped section from 11½" diameter circle equal to area difference of circle and sphere. formed by preheating sheet to 200°F. and vacuum bagging.	OK except for slight excess of material at end of V cut.

1-3.5 Discussion of GE's Evaluation of ABL-15:

Vacuum Bag Forming: As can be seen in Table 5 the ABL-15 did not have sufficient internal flow to allow the cork particles to move to the degree necessary to compensate for the reduction area required to go around the bottom of the hemisphere with vacuum pressure alone. However, the data does indicate some shapes or curvatures could be vacuum bag molded since the top 2/3 - 3/4 of the hemisphere could be molded with the vacuum bag alone. What the exact limitations are for this formula could not be ascertained for the amount of money involved in this contract.

Mold Ring Forming: Referring to Table 5, several parts were formed using the molding ring. Table 5 shows that the application of pressure via the molding ring produced good parts when done smoothly and slowly over preheated sheets and mold. The sheet material became considerably weaker when heated, and this caused tears and breaks in the first parts made when pressure was applied rapidly. Interestingly, water soaks of the "B" staged sheet permitted forming of a part in a one-step gradual operation. The cured part subsequently appeared to be equal in quality to the good ones made by the previous procedure.

Vacuum Bag Molding with Excess Removed: The vacuum bag technique was effective in forming the ABL-15 sheet over the 9" hemisphere when an excess of material was removed. The excess material in this cure was the difference in area of a circular sheet and the area of the sphere it would cover (8.85 sq. in.). The sheet had sufficient formability to form over the sphere and close the gap. subsequent curing while the part was vacuum bagged produced a fixed shaped part. In the part made this way there was a slight excess of material at the apex of the triangular shape that had been removed. This could be eliminated by a minor change in the shape and amount of material removed. This technique would lend itself to the die-cutting of repetitive parts.

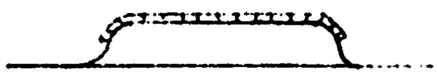
In all molding techniques for ABL-15, a $\frac{1}{4}$" thick sheet is approaching the maximum thickness that can be readily processed.

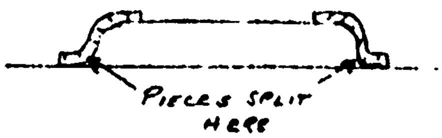
NASA Part: The results of the experiment with this part are described in Table 6. A 90° angle between the flange and the domed section caused separation in the cork sheets at this point. For this reason two cork sheets must be formed separately, one for the domed section and a second for the flange. A composition adhesive may be advisable at the joining interface, if high heat loads are liable

Table 6

NASA Form

Sheet ID	Density	% Wt. Lost	Procedure	Results
2,D	25.8	14%	Cut 11-7/8" circle preheat sheet at 200°F for 5 min., then vacuum form over NASA dome at 200°F. Cure 300°F for 30 min.	OK
3,D	26.6	--	Cut into 2 rectangular strips 3" wide x 9" long. Soaked one in water for 1 hr. Place both over flanges of NASA dome and vacuum form at 200°F - 30 min., 300°F - 30 min.	Both pieces cracked at flange radius.





to occur at that location.

Overall Evaluation of ABL-15 by GE: "Based on the results of this small program involving formability evaluations and limited tests, Dodge Cork Company,Inc. has prepared a quality "B" staged cork composition that - with proper techniques - can be formed over complex curved surfaces."

Area 2: Comparison of Moldable Cork to Existing Cork Ablation Material

2-1 Existing Specifications:

Incorporated into our contract were portions of the existing specifications for cork ablation material. These specifications were to be goals rather than specific requirements, in that we were unsure whether we could make any moldable cork sheet let alone one which could meet every specification already in existence. In addition it should be noted that these specifications were written by Armstrong Cork Co., in 1963 and their relevance to present day systems or to specific applications has not, to our knowledge, been recently investigated. The specifications included in the contract were:

Properties	Requirements
Density (pcf.)	15 - 30
Tensile Strength (psi.)	250 min.

Tensile Elongation (%)	13 min.
Compression Set (%)	23 max.
Specific Heat (BTU/lb./°F.)	.40 min.
Thermal Conductivity at 100°F. mean temp. (BTU/hr./ft^2/°F./in.)	0.6max.

2-2 <u>Evaluation of ABL-15 Material</u>:

As specified in the contract Dodge manufactured 300 lbs. of ABL-15 a sample of which was submitted to General Electric Space Center at King of Prussia, Pa. for evaluation. The results and procedure are listed in Table 7.

Table 7

THERMAL AND MECHANICAL PROPERTIES
(ABL 15 PRODUCTION LOT 1)

THERMAL

The three sets of samples were preconditioned 16 hrs. at 220°F before the measurements were performed. The thermal conductivity measurements were performed in accordance with ASTM-C177-63 using the Dynatech Guarded Hot Plate, and the Perkin Elmer DSC-2 at 100°F. Specific heat was measured at 150°F with the Perkin Elmer Differential Scanning Calorimeter. The specific heat was determined at a heating rate of 10°C/min.

SPEC. #	(lb/ft^3)	T (°F)	K ($\frac{Btu}{ft\ sec\ {}^oF}$)	K ($\frac{Btu\text{-}in}{ft^2\ hr\ {}^oF}$)	C_p@150°F $\frac{Btu}{lb\ {}^oF}$
1	25.2	102 100	$1.01 \cdot 10^{-5}$ $1.07 \cdot 10^{-5}$	.436 .462	.387
2	24.9	99	$1.06 \cdot 10^{-5}$	.458	.408
3	25.0	100	$1.05 \cdot 10^{-5}$	.454	.409
Av $\pm$ 1σ	Av = 25.0$\pm$.15		Av=$1.05 \cdot 10^{-5}$ $\pm .03 \cdot 10^{-5}$	.453$\pm$.010	Av = .401$\pm$.012

MECHANICAL

Compression Set
(Dodge Cork Co., Inc. Procedure)

Sample	Percent
1	34.5
2	36.0
3	35.4
Av =	35.3 $\pm$ .7

Table 7. (Cont.)

	Sample	
Tensile Strength, psi.	1	425
	2	358
ASTM D1170-62T	3	402
	4	381
(Sample Size 2" x 6")	5	382
	6	345
	7	378
	8	372
	9	349
		AV = 377±25
Tensile Elongation (%)*	1	5.0
	2	4.4
	3	4.9
	4	4.7
	5	5.0
	6	4.8
	7	5.0
	8	5.0
	9	4.9
		AV = 4.86

*Corresponding to strain at peak tensile stress.

2-3 Discussion of Results:

As can be easily seen by comparison of Table 7 with the properties listed in section 2-1, the ABL-15 performed quite well for an experimental formulation. While it fell below standard in compression set, and tensile elongation, it was superior in tensile strength and thermal conductivity. It stayed about the same in specific heat. In addition the average density of the material is 5 pcf. lower than the existing compositions, which could be significant in payload considerations. While heat of ablation tests were not run under this contract, it is our verbal understanding from Mr. H.M.Walker, that a radiant heat of ablation was run with ABL-15 in comparison to P-50 (Sheller-Globe material) with no discernable difference between the materials.

At the risk of going beyond my expertise, I question the significance of the compression set and tensile elongation requirements for an insulating material. In any case, we were quite satisfied with ABL-15 performance at this stage of development.

Area 3: Production Methods and Difficulties

3-1: Actual Production Run

3-1.1: In that our contract only provided enough money for one actual production run, there was virtually no opportunity for controlled experimentation in the production environment. Four, 100 lb. mats, $28\frac{1}{2} \times 50\frac{1}{2} \times 4\frac{1}{2}$" were manufactured using Dodge's present equipment and processing. These mats were mixed in a 250 gal. Sigma bladed overarm mixer (1925 vintage). The mix was pre-weighed then screened into steel molds to remove any "resin balls". The mix was pressed approximately 1/3 of its initial volume into the mold by a hydraulic ram, the mold sealed, then baked in gas fuel ovens.

3-1.2: Observations on Production Methods: While the production ran rather smoothly, several areas for improvement were readily observed. Dodge is primarily a gasketing manufacturer. While Dodge has maintained an excellent reputation for quality in this field, the need for very highly controlled production is not generally required in gasketing material. A relatively wide range of values is industrially acceptable on the requisite properties. This may not be the case with the ablative material. It should be noted that Armstrong built a special production line just to handle its 2755 material. Thus, while we are confident that we can make a product that would conform to the high standards that might be needed for an ablative material, some modification of existing facilities would probably be necessary. The difficulties are as follows:

(a) Mixer: The present mixer is a low capacity mixer which after 50 years of use does not have the shear action it should. Thus when using a fine grain of cork, such as the type used in ABL-15, a small amount of "resin balls" are formed, and not broken up in the mixer. Dodge is prepared to either modernize or replace this mixer, if the moldable cork concept is accepted by NASA and the return or investment justifies the expenditure. Naturally a more efficient, larger mixer would yield a greater quantity of good material, thus reducing the cost to NASA.

(b) Molding: There are two major problems in molding this material. The first is a rather simple one, namely the extra labor burden of cleaning the mold properly. Since the ABL-15 contains an unusually high resin-cork ratio, a certain amount of resin is squeezed onto the molds, thus necessitating daily cleaning of the molds, a process not required by our other items. The second problem is more complicated. The cork mix does not act as a hydraulic fluid, thus, when pressed, a rather significant density variation appears in the 4½" mat. This variation is graphically represented in Table 8. In addition the molds presently used are not particularly tight fitting, thus a certain amount of material leaks out leaving some low density areas around the edge, causing a small amount of finished material to be unusable. The first problem, of course, can be solved simply by considering the extra labor within the final cost. The second has two possible solutions. The first is to determine how significant the density variation really is in terms of the end application. Is a tight cluster of density really necessary for the performance demanded by NASA? If it is necessary, then Dodge will have to explore various engineering methods to improve the consistency of the final product.

(c) Baking: Since the degree of "B" staging of the resin is crucial to the moldability of the ABL-15 formulation, baking time and temperature control are important variables. The ovens presently used by Dodge are likewise quite old and thus are not exactly perfect in their heat distribution within the oven. Also, the ovens are in banks, so, when an adjacent oven is on or off, it affects the condition in the next oven. This is significant in that the molds cool inside the ovens, thus a variable in cool down temperature is introduced when the adjacent oven is on or off. Dodge would again be willing to invest in one or more new ovens to better control the degrees of cure of an ABL-15 type material, if the investment could be justified.

(d) Splitting: The material was split into various thicknesses by use of a Feken-Kirfel band knife block splitter. No problem was incurred during this process. Sheets of 1/8", ¼", 3/8", and ½" were split. However, the nature of this type of splitting requires a certain amount of wastage, usually about 7-10% of the original volume of material.

3-2 Storage and Shelf Life

3-2.1 In that the degree of "B" staging is crucial and that the resin will advance at room temperature careful consideration to methods of controlling the advancement must be considered. While the experimentation in this area is far from complete, both Dodge and GE did try to establish some rough parameters. The results of these experiments are listed on Table 9.

3-2.2 Discussion of Results:

The data indicates that while care must be taken to store the material at refrigerated conditions, there is some latitude in its usage. Especially interesting is the fact that when the volatiles are sealed in with poly bags the material retains its liveliness over a relatively long

TABLE 8

DENSITY DISTRIBUTION WITHIN 28"x50"x4½" BLOCK OF ABL-15 CORK

BLOCK #3
MOLD DATE 6/30/77
TEST DATE 6/30/77

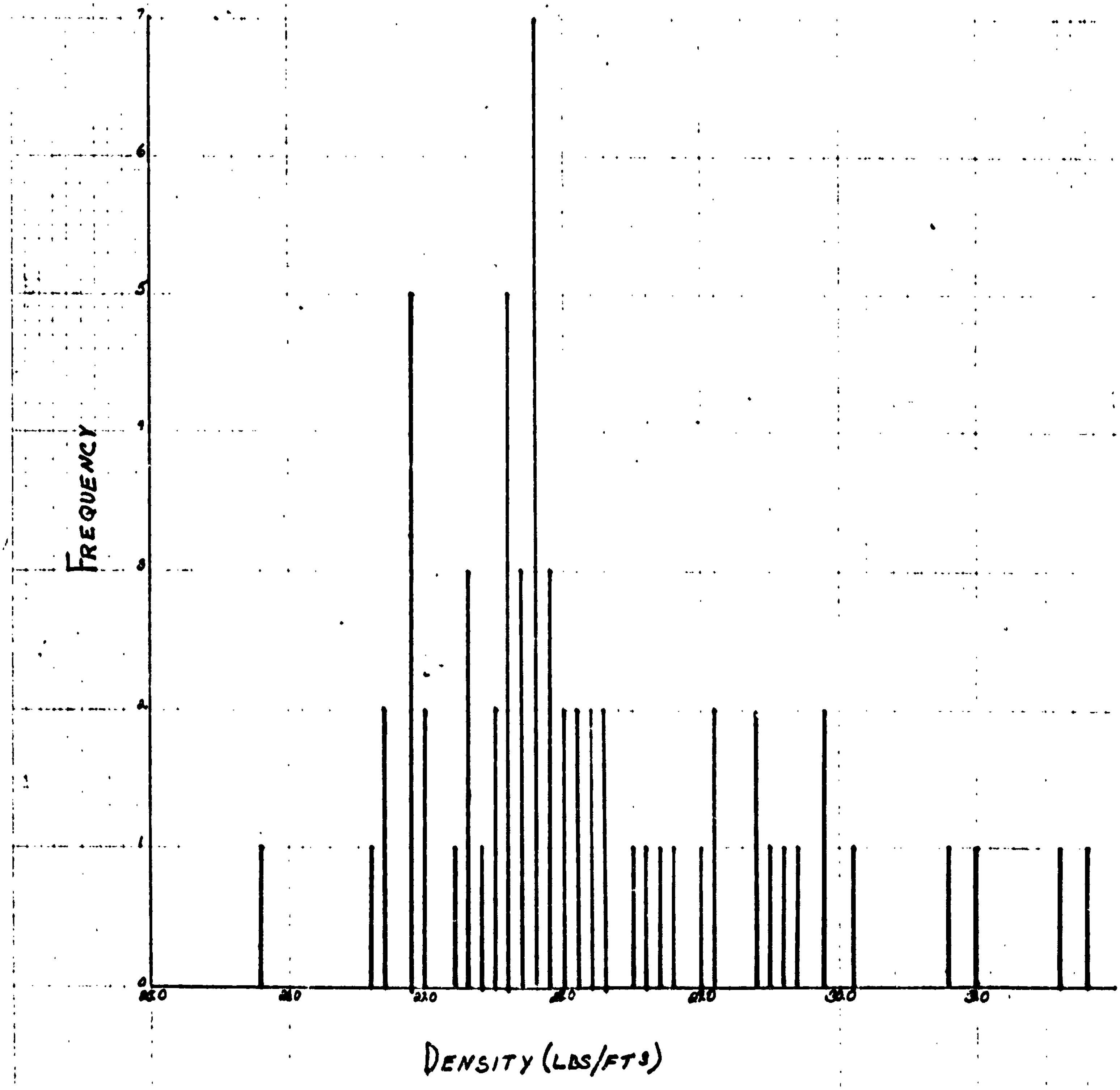


Table 9

All pieces from ABL-15, Lot #3. All pieces conditioned at ambient temperature (70°F +5°) and ambient humidity (55+5%). All pieces were formed over 4½" diameter hemisphere. Sheets were cut into 5" diameter circles, then formed with one stroke using plastic molding ring.

I. D. #	TIME CONDITIONED	RESULTS
1	1 HOUR	Sheet molded without heating. Was moldable with some difficulty. Showed very fine surface cracks.
2	3 HOURS	Surface somewhat dryer. Severe surface cracking when molded, without being heated.
3	3 HOURS	Sheet heated to 175°F for 3 min. Moldable with fine surface cracking.
4	5½ HOURS	Surface felt dry. Sheet heated at 175°F for 4 min. Moldable with larger surface cracks than #3.
5	8 HOURS	Surface very dry. Sheet heated at 175°F for 8 min. Molded with difficulty. Sheet had same degree of cracking as #4.
6	24 HOURS	Sheet hard. Too brittle to be molded even with heating.

Table 9 (Cont.)

Sheet Storage

I:	R.T., exposed to Atmosphere:	.5 days = -13% wt. (stiff)
		10 days = -14% wt.
II.	R.T., wrapped in P.E.:	5 days = -2% wt. (flexible)
		10 days = -2% wt. (")

period of time even at room temperature. More work should be done in this area to establish exact parameters for ABL-15 usage in the factory and on the job site.

3-2.3 As a secondary note, it is likely that Dodge will have to expand its cold room storage space if full production of this type of material becomes a reality. Also NASA and Dodge will have to decide if refrigerated transport of material from Lancaster to NASA fabrication facilities is necessary.

3-3 Costs:

At this point in time, it would be very difficult to define an actual cost to NASA for full production of an ABL-15 type material. The changes in production methods that might or might not be necessary as discussed in section 3-1.2 would cause a difficult-to-predict variation in actual costs. Secondarily the quality control standards will have to be established which would define the percent of good material obtained from the total production. This, likewise, is a difficult-to-predict addition to the base cost. In essence, too much remains undecided to clearly spell out a projected cost. However, based on our long experience in the manufacture of cork products, I do feel we could probably produce the product within the same range as the present P-50 formulation which works out to about $70.00 per inch of a 28" x 50" block.

Overall Summary and Suggestions for Further Experimentation

In summary, we at Dodge, were pleased with the progress made under this contract. Exploring pretty much uncharted areas, we were able to obtain a potentially useful product. We did establish that, in fact, a moldable cork sheet was a realistic product. We did manufacture, on existing equipment a moldable material which did exhibit most of thedesirable characteristics needed in a successful thermal ablation material. Still,despite our progress, much remains to be explored. We see further experimentation to lie in these major areas: (1) refining and characterization of the existing ABL-15 formula in order to qualify for use in NASA vehicles, and (2) new techniques or modification of ABL-15 to improve specified properties. In each area I would suggest the following:

(1) Refining and Characterization of Present ABL-15:
Our original experimentation left certain questions unanswered. Further work should be done in better defining: initial cure time, maximum self life, best conditions for reducing resin advancement during the stages of processing, effect of various cork-resin ratios on final properties, methods of final curing (either in place or on preconstructed molds), molding techniques, adhesive compatability, effect of cork grain size on final properties, modes of transportation,

techniques to reduce density spread within sheets, performance of material in different thicknesses and over different complex surfaces. In addition more precise standards for qualification of this material must be established. The requisite tensile strength, elongation, thermal conductivity, etc. must be clearly defined for this product. We at Dodge think at this point it would be advantageous for both us and NASA, to have some ideas where and how this material might be used in NASA's program. This would allow us to direct further research into fruitful channels. The more input and direction we receive, the more we can tailor our formulations to conform to NASA's needs.

(2) New Techniques and Modifications:

Several suggestions come to mind to expand the technology generated by this contract. Dodge presently makes material in continuous roll form. Perhaps, the ABL-15 can be modified to allow it to be molded and split into 50" x ⅛" x 200' rolls. This might offer some advantages in covering large surfaces.

In the course of the experimentation it was observed that the area that came in contact with the aluminum retaining ring used for molding formed a hard "slick" surface, probably caused by migration of the resin to the cork surface in contact with heated metal. Perhaps a molding technique incorporating this phenomena might offer some advantages. Other ideas include adding rough fibers to the cork-resin mixture to increase strength of the partially cured sheet, exploring the effectiveness of layering thin cork sheets to allow for application in severely angled areas, further exploration of use of castable resin systems as tried in the ABL-14 formulation, perhaps in conjunction with a scrim cloth, exploration into the use of more compressible formulations, which might be more "energy absorbing".

We at Dodge are proud of our progress and wish to provide any follow-up assistance that NASA desires.

Terry S. Hyman
Project Supervisor
12 August 1977