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FINAL REPORT

November 8, 1967 - April 30, 1969

Prepared by:

Glenn K. Armstrong

Prepared for:

Manned Spacecraft Center
NATIONAL AERONAUTICS & SPACE ADMINISTRATION
Houston, Texas 77058

June 1, 1969

Progress through Research

DYNATECH

DEVELOPMENT OF NONFLAMMABLE PAPER CONSTRUCTIONS

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Dynatech Report No. 870

June 1, 1969

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Progress through Research

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Section 1
SUMMARY

This report summarizes the work done at Dynatech R/D Company under Contract NAS 9-7610, "Development of Nonflammable Paper Constructions." The objective of this program was to develop a writing paper that would be nonflammable for use in category A, MSC-A-D-66-3-A. Previous work at Dynatech R/D Company with microfiber glass paper constructions indicated that it would be possible to modify the soft absorbent glass paper to obtain inorganic based sheets that closely resembled conventional cellulose based writing paper. Consequently, a development program was initiated to achieve such modified microfiber glass based sheets.

There are a number of inorganic fibers which can be processed on conventional papermaking equipment to form a highly entangled mat resembling cellulose paper, but the sheets formed are weak, have low tear strength, do not print well, and most inorganic papers use a binder to obtain sheet strength since the fibers do not form hydrogen bonds at their points of contact as cellulose fibers do. The tensile properties of the sheet are determined by the cooperative behavior of binder and fibers, with failure usually occurring in the binder since it is, in most cases, an organic material with structural properties inferior to the inorganic fibers. Nonburning, inorganic cements produce high bond strengths but produce brittle papers with poor tear strength. Tear properties depend on the sequential transverse failures of the fibers which must be well anchored and not pull loose before failure. Long fibers usually increase tear strength by providing a large number of attachments. Since most inorganic fibers have smaller elongations at break than do cellulose fibers, rubbery binders which permit some relative fiber movement and, hence, more work to break, usually increase the toughness.

Sheet development during this investigation centered on the use of three fibrous inorganic nonburnable base materials for the paper. These were asbestos, microfiber glass, and beta glass. Additions of other low flammability fibers such as PBI were investigated as a means to increase crease resistance. Low flammability fluorinated polymers such as Fluorel and Kynar were investigated as binder materials.

Various blends of glass microfibers, asbestos, and chopped beta glass were made into hand sheets and evaluated as possible paper replacements. A blend (by weight) of 25% long fiber chrysotile canadian asbestos, 25% short fiber asbestos (Union Carbide-Coalinga Type), 25% 104 type microfiber glass (Johns-Manville) and 25% chopped beta glass (Owens Corning) was stronger and more tear resistant than previously reported inorganic papers, with a tensile strength of 840 psi and an Elmendorf Tear of 100 gm. When impregnated with 7.5% weight add on of Kynar vinylidene fluoride resin the tensile strength increased to 1040 psi but the tear was reduced to 80 gm. This formulation, designated Dynapaper, closely resembled buff colored writing paper but was somewhat deficient in tear strength, had poor crease resistance, but did not ignite in 16.2 O_2.

The promising characteristics of these sheets were further developed during the contract extension period. One approach involved using organic fibers with low inherent flammability blended with the basic inorganic formula to increase tear strength and improve crease resistance.

A 50% blend of chopped PBI fibers and the inorganic Dynapaper when made into a sheet and impregnated with 27.5 wt. % Fluorel (Raybestos Manhattan L-3603-6) had a tensile strength of 1590 psi and an Elmendorf tear of 220 gm. The crease resistance was improved, but the brown PBI fibers caused a mottled appearance which was objectionable.

Blends of Dynapaper and combustible fibers such as nylon, Dynapaper and Dacron and Dynapaper and cellulose were prepared. 50% cellulose-50% Dynapaper was impregnated with diammonium phosphate (DAP) and over-coated with Fluorel. Consistent results were not obtained in flammability tests but one sample with 18.5% DAP added plus 18% Fluorel further added was self-extinguishing in 6.2 psia 100% oxygen.

Further development of cellulosic based systems is recommended, especially since the harsh requirements of 16.2 psia pure O_2 have given way to 6.2 psia. For example, at this lower total oxygen pressure a sample of 100% cellulose blotter material was found to be self-extinguishing with 36% add on of diammonium phosphate overcoated with 8.1% Fluorel.

Nomex spunbonded paper posses outstanding tensile and tear strength compared to cellulosic based sheets. With a coating of 12% Borax-boric acid overcoated with 8% Fluorel the burn rate in 6.2 psia O_2 was only 0.33 in/sec. Thus treated Nomex paper should be a candidate for further development as a nonburning, strong, lightweight paper replacement if the flammability can be further reduced.

Sheets of paper which used glass scrim as reinforcement and Dynapaper furnish as the basic stock were prepared. Some problems were encountered in one-sideness and delamination; however, the resulting sheets had unusual tear and tensile strengths. With further development, these scrim reinforced structures should be excellent candidates for flight paper.

The unimpregnated asbestos glass based paper developed during this program, while not suitable for writing paper, represents a high temperature paper structure of higher strength than any previously reported in the literature. Samples of this material are available for test in other applications.

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Section 2
INTRODUCTION

The objective of the development program reported here was to produce an inorganic, noncombustible flight paper comparable to conventional cellulosic papers in strength and printing qualities. Papers composed wholly of glass fibers of submicron diameter have been prepared in past work at Dynatech Corporation. Recognition of the potential for improvement of these sheets led to undertaking the work reported here.

Present Technology of Papers Composed of Inorganic Fibers

There are a number of inorganic fibers which can be processed on conventional papermaking equipment to form a highly entangled mat resembling cellulose-paper, but the sheets formed are weak, have low tear strength, and do not print well. Also, most inorganic papers use a binder to obtain sheet strength since the fibers do not form hydrogen bonds at their points of contact as cellulose fibers do.

Substantially all the prior work to strengthen sheets composed of inorganic fibers has been carried out with flammable binder materials. It is reasonable, that sheets containing only a small proportion of flammable binder might be nonflammable in practice. However, the stringent flammability requirements for the paper under development limits the binder levels to quite low proportions.

The tensile properties of a sheet are determined by the cooperative behavior of binder and fibers, with failure usually occurring in the binder since it is, in most cases, an organic material with structural properties inferior to the inorganic fibers. Nonburning, inorganic cements produce high bond strengths but produce brittle papers with poor tear strength. Tear properties depend on the sequential transverse failures of the fibers which must be well anchored and not pull loose before failure. Long fibers usually increase tear strength by providing a large number of attachments. Also most inorganic fibers have smaller elongations at break than do cellulose fibers and rubbery binders which permit some relative fiber movement and, hence, more work to break, usually increase the toughness. Thus nonflammable binders occupy a key position in this specialized development.

Inorganic fibers of glass and asbestos were selected as the initial candidates for this development since they are noncombustible, widely available, inexpensive, and considerable technology exists on their manufacture on conventional papermaking equipment. Although a number of asbestos papers are on the market, very little has been written about their preparation and properties. U.S. Patent 2,772,157 does cite the advantages of mixing glass and asbestos fibers to produce smooth, strong, high-temperature resistant water-laid felted fibrous sheets, but no definitive articles were found in the open literature relating to asbestos paper manufacture. In contrast, glass fiber papers have been extensively studied. For example, Huckaba and Geddes (3) have studied the preparation of paper made entirely of glass fibers (without any organic binders) and showed that production of high-quality glass paper requires optimization of both fiber length distribution and control of the pH of the stock. These authors also conclude that tensile strength is apparently derived from both intermeshing of fibers and chemical bonding due to the adhesive action of the gelatinous silicic acid formed from the reaction of the glass fines with the mineral acid which is used to aid dispersion. They prepared papers with tensile strengths as high as 560 psi.

However, organic binders are usually used to further enhance the tensile strength of glass fiber sheets. Callinan and Lucas (1), two pioneers in the development of glass microfiber paper, prepared glass fiber papers by adding organic binders to the beaten fibers. The levels of binder used range from 8 to 84%, and the best sheet tensile strength was 512 psi with 11% addition of Marco polyester resin. They also used bentonite clay as an inorganic binder and prepared a brittle, 20% bentonite 80% glass sheet which had a tensile strength of 386 psi. Post impregnation of this sheet with an acrylic resin produced a paper with a tensile of 1,890 psi.

Binders

Inorganic papers must use some type of a binder to obtain sheet strength because the fibers do not fibrillate and form hydrogen bonds at their points of contact, like cellulose fibers. Also, the stringent flammability requirements of MSC P-AD-67-13 dictate the levels or organic binder that can be used. Binder characteristics which lead to high sheet strength are listed by Hentschel (2) as follows:

1. A good adhesive bond with the fiber. This is generally favored by chemical similarity between the binder and the fiber, although it is not a strict requirement.

2. Toughness and deformability. This is favored by the more rubbery polymer states: amorphousness and copolymerization.

3. The ability to form thin films between the surfaces being joined. This is favored by fluidity in the system as the bond is being formed.

Hentschel has also studied the effect of binder content on sheet strength and Figure 1, taken from his article shows this relationship.

This figure shows that maximum properties are reached at 20-30% binder. At these levels, binder flammability becomes of major concern and a trade-off exists between sheet properties and the binder levels necessary to obtain a nonflammable structure. With such severe limitations on binder content it is desirable to concentrate the binder at the fiber junctions to obtain the optimum strength. Under these conditions, a flame front will not propagate in such a sheet if the ratio of the heat of combustion of the binder to the specific heat of the total sheet were such that combustion of a portion of the flammable constituent would not furnish sufficient heat to ignite an adjacent section of the sheet.

The physical and mechanical properties of the binder are very important. Nonburning inorganic cements produce high bond strengths, but the papers are brittle and have poor tear strength. A deformable binder can accommodate itself to deformation without brittle failure, and rupture can be made to take place in the fiber, rather than in the binder. Thus the degree of success in obtaining the ultimate properties from a given fiber will depend on obtaining a nonburning elastomeric binder. Hentschel gives a formula to calculate the absolute level of sheet strength that can be expected from a well bonded system. This is:

$$\text{Sheet tensile strength} = 3.7 \times \text{fiber tenacity}$$

Where sheet tensile strength is in units of lb/in/oz/yd^2 and tenacity is measured in gm/denier. For example, this formula predicts that a sheet formed from beta glass should have a tensile strength of 23.2 lbs/in. for a 4 mil thick sheet. Bond cellulose

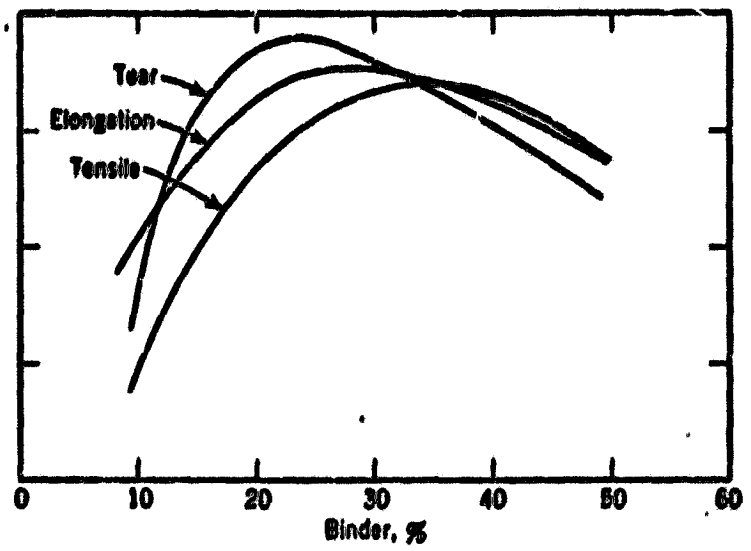

Figure 1. Physical Properties of Paper as a Function of Binder Level

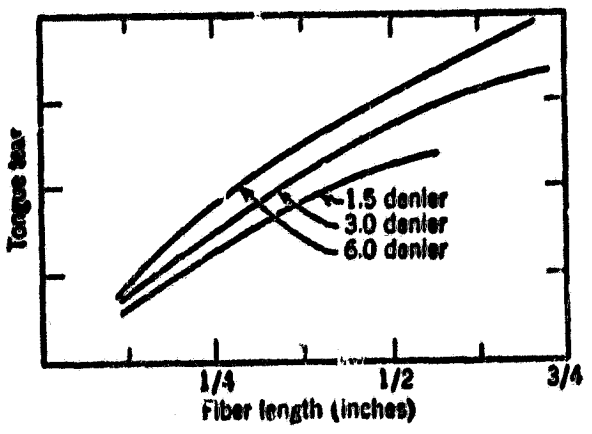

Figure 2. Tear Strength of Paper as a Function of Fiber Length and Diameter

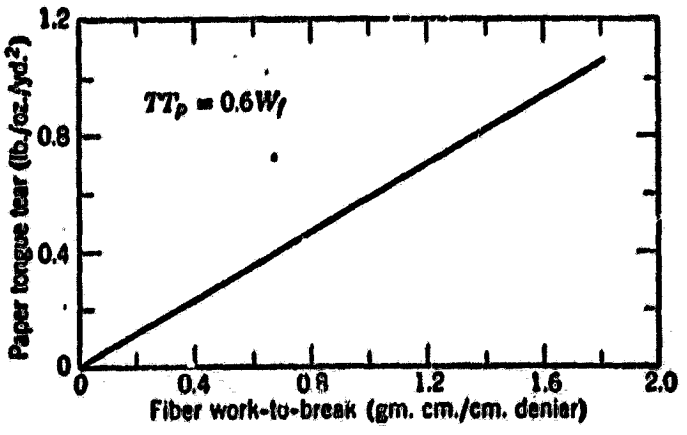

Figure 3. Tear Strength of Paper as a Function of Fiber Toughness

papers, by comparison, have a tensile strength of 10-14 lbs/in and, to match these properties in the inorganic sheets, binder levels of about 15% would be required. Such values are not unreasonable and indicate the possibility of fabricating an inorganic paper which will have the required tensile strength.

Another important requirement for the noncombustible paper is high tear strength since pages of flight data books are bound with rings and the paper must not tear in the area around the hole. Most microfiber glass papers examined had low tear strengths and permit the easy propagation of a tear, once tearing has begun. Hentschel (2) has examined the fiber properties contributing to tear strength, and his general relationship relating fiber diameter and length is shown below. Empirically it has been shown that fiber work-to-break correlates most closely to sheet tear strength as shown in Figure 3. Thus, long fibers with a high work to break are required to produce papers with good tear strength and the longest, toughest, nonflammable fibers that can be processed and still give good sheet formation are desired.

Although the generalized correlations are useful guides, it is difficult, at the present state of the art, to generalize about the properties of papers made from blends of various fibers as used in this work.

Section 3
PROCEDURE

3.1 Fiber Dispersion Technique

Hand sheets were prepared and tested using techniques which are standard in cellulosic based sheet development work.

The basic fibrous raw materials were dispersed in a laboratory sized beater, shown in Figure 4. Since inorganic fibers do not defibrillate in the same manner as cellulose fibers, long beating times were avoided. Typically, dispersion was obtained by beating with the bed plate of the beater either lightly touching the knives or with a clearance of 2-5 thousandths of an inch. Dispersions of 1% by weight of the fibers in water could be obtained in 5-10 minutes with these bed plate clearance settings.

3.2 Hand Sheet Production

Weighed quantities of the fiber furnish were changed to a standard sheet mold and processed into hand sheets. Both an 8" and a 12" square mold were used. Figure 5 shows a hand sheet being removed from the 12" mold.

3.3 Saturation Technique

The Kynar samples were first saturated with a 30% solution of Kynar in acetone, then placed between two sheets of dry white blotting paper and squeezed through a set of soft rubber rolls. This procedure improved the surface smoothness and printability of the paper and left the surface dry and not wet with the impregnating solution, as was the case when the blotters were not used.

3.4 Physical Measurements

The tensile strength, Elmendorf tear and thickness of a sample was measured according to the standard TAPPI methods, T 404, T 411, T 414.

3.5 Documentation of Raw Materials

The raw materials used and their commercial suppliers are listed below.

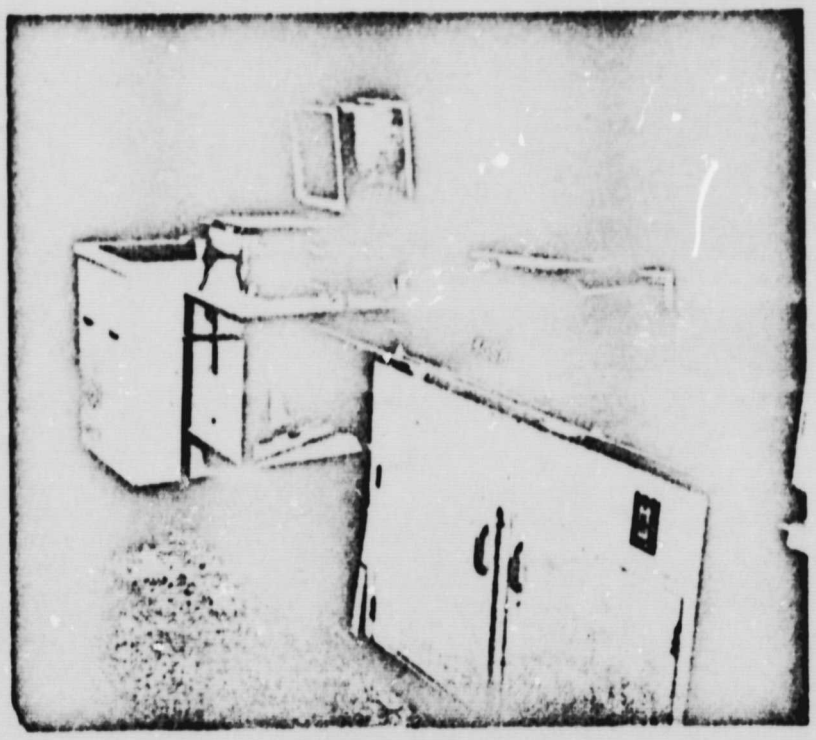

Figure 4

Arrangement of Beater and Sheet Mold

Figure 5

Hand Sheet Mold

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Asbestos - Chrysotile

Colloidal grade Coalinga asbestos	Union Carbide Corp. 270 Park Ave., N.Y., N.Y.
Lake Asbestos - 3T grade	American Smelting and Refining Co. 120 Broadway, N.Y., N.Y.

Glass Fibers

104 grade glass microfibers	Celite Div. Johns Manville 22 E. 40th Street, N.Y., N.Y.
Chopped beta glass fibers	Owens-Corning Fiberglas Corp. Ashton, R.I.

Polymeric Materials

Kynar vinylidene fluoride resin	Pennwalt Corp. 3 Penn Center Philadelphia, Pa.
CNR Rubber Soln.	Thiokol Chemical Corp. Denville, N.J.
Glass Resin - 100	Owens-Illinois 1700 N. Westwood Ave. Toledo, Ohio
Gayco FR 86-KV 19139 Coating Solution	Gates Engineering Co. 100 S. West St. Wilmington, Delaware
Fluorel L-3203-6 Coating Solution	Raybestos-Manhattan Corp. North Charleston, S. C.

Section 4

RESULTS AND CONCLUSIONS

4.1 Basic Inorganic Fiber Studies

The basic sheet forming material used for this developmental program was 104 glass microfibers. It is possible to process submicron glass fibers into paper type structures using conventional papermaking equipment. However, the sheets that are formed resemble filter paper in their properties and are quite weak and not suitable as writing papers. By blending asbestos with the glass, sheets more closely resembling paper can be produced. However, these sheets have poor tensile strength, low tear strength, and require the addition of organic binders to attain strength levels similar to those of cellulosic based sheets. A considerable portion of the development work in this program was centered around improving the basic properties of the glass-asbestos based fibrous sheets, since this mixture was thought to have the best chance of meeting the 16.2 psia pure O_2 flammability test.

4.2 Effect of Additives on Sheet Tensile Strength

The addition of asbestos to the microfiber glass results in sheets with much more "hand" and rattle with greatly improved surface qualities. The effect on basic sheet tensile strength by adding colloidal asbestos to both beta glass and 104 glass is shown in Tables 1 and 2.

The strengthening of the sheet is more marked with the beta glass than with the 104 glass, however, sheets of all beta glass do not have good surface properties and some of the finer diameter 104 glass is beneficial in improving the appearance of the sheets and making them more paper-like.

Table 3 shows the effect on sheet tensile strength of various blends of both 104 and beta glass when added to 50% colloidal asbestos. Maximum sheet properties were obtained at an equal mixture of the 104 and beta. The basic sheet forming tendency of 104 glass is excellent. With only a minimum of processing, well formed sheets are produced and the drainage rate on the screen is quite high, even if the

Table 1

Effect on Tensile Strength of Additions of
Colloidal Grade Asbestos to 104 Glass Sheets

% 104 Glass Fiber	% Colloidal Asbestos	Tensile Strength psi
100	0	60
60	40	100
50	50	100

Table 2

Effect on Tensile Strength of Additions of
Colloidal Grade Asbestos to Beta Glass Sheets

% Beta	% Colloidal Asbestos	Tensile Strength psi
100	0	100
50	50	100
34.7	65.3	270
26.5	73.5 *	350

*at higher asbestos loadings the sheet did not possess enough strength to be couched from the wire

Table 3

Effect on Tensile Strength of Additions of
104 Glass and Beta Glass to a 50% Colloidal Asbestos Sheets

% Colloidal Asbestos	% 104 Micro Fiber Glass	% Beta Glass	Tensile Strength
50	50	0	100
50	37.5	12.5	100
50	25	25	325
50	12.5	37.5	200
50	0	50	100

Table 4

Effect on Sheet Tensile Strength of Blends of Various Inorganic Materials

Sample No.	Weight % of Component in Final Sheet						Retention of Mixture on Screen %	Sheet Thickness mils	Tensile Strength Dry Sheet psi
	104 Glass	Beta Glass	Kaolin Clay	Attapulgite Clay	3T Canadian Asbestos	Coalinga Colloidal Asbestos			
1	0	29.4	62.8	0	0	7.8	63	3.5	140
2	0	42.9	36.6	0	0	20.5	94	3.0	370
3	0	26.1	48.8	0	0	25.1	52	3.8	320
4	0	26.1	0	48.8	0	25.1	51	4.0	330
5	35	0	30	0	0	35	62	5.0	200
6	40	0	0	20	40	0	96	8.0	330
7	40	0	0	20	0	40	87	5.5	330
8	0	50	0	50	0	0	47	3.0	160
9	50	0	0	0	50	0	92	6.0	330
10	50	0	0	50	0	0	73	3.5	340
11	50	0	0	0	0	50	90	5.0	130
12	0	50	0	0	0	50	83	3.8	580
13	0	50	0	0	50	0	93	5.0	340
14	100	0	0	0	0	0	--	7.0	60
15	60	0	0	0	0	40	--	8.5	190
16	37.5	0	0	37.5	0	25	--	8.5	350
17	15.8	0	0	84.2	0	0	--	5.5	550
18	25	25	0	0	25	25	96	4.5	890

microfiber glass is beaten for an extended period and many "fines" are produced. In these inorganic structures fines act as a gluing agent to increase sheet tensile strength. Thus some beating or chopping of the glass fiber is necessary if higher sheet tensile strengths are desired. However, beating degrades fiber length and tear strength so extended beating times are detrimental if high tear strength is desired. Experiments were conducted with other materials as a possible source of the fines to see the effect on sheet tensile strength. Two clays - a kaolin with plately shaped particles, and attapulgite which has a fibrous shaped particle, were evaluated. The results of these blending tests are shown in Table 4. The tensile results show that clay is useful in providing a source of the fines and its addition to the asbestos-glass also gives sheets with good surface properties. However, clay makes the sheet more brittle and, as shown by blend 18, the best sheet strength properties were obtained without the use of clay.

4.3 Optimization of Both Tensile and Tear Strength

Since formula 18 had very promising properties, a further investigation of the tear properties of this mixture was made. The original sheets as listed in Table 4 were prepared from materials that were well dispersed. The beating procedure used is shown in line 3 of Table 5. During the investigation of beating variables, it was found that the 104 microfiber glass acted as a dispersing aid for the beta glass and excellent dispersions of both types of glass could be obtained in shorter times if the two materials were beaten together. High shear dispersion in a Waring blender was detrimental since it reduced fiber length and reduced final sheet tear strength. Beating in the chest beater with light pressure on the bed plate for as long as an hour produced sheets with smoother surfaces and higher tensile strengths, but these sheets had poorer tear strengths than the sheets made from materials beaten only 30 minutes. Longer beating times produced fine particles and reduced the fiber lengths. As expected, the presence of fines increased the tensile strength, but at the expense of decreased fiber length which decreased the tear strength. A mixture of the 104 glass and Beta glass was found to give the best balance of surface and strength properties to sheets manufactured from these materials when they were compared to sheets made from either constituent alone. Apparently, the 104 glass furnished the fines and the beta glass, when beaten just enough to provide good sheet

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Table 5

Effect of Preliminary Beating of Raw Materials On Final Sheet Properties

	Formula	Treatment	Formation Visual	Elmendorf tear, gms	Tensile psi
1	25% Lake Asbestos	A	Poor - Strings of asbestos and undispersed Beta glass	60	730
	25% UC Asbestos	B			
	25% 104 Glass	A			
	25% Beta Glass	A			
2	25% Lake Asbestos	B	Beta Glass undispersed	--	820
	25% UC Asbestos	B			
	25% 104 Glass	A			
	25% Beta Glass	A			
3	25% Lake Asbestos	C	Good formation - Slow drainage rate on screen	40	890
	25% UC Asbestos	B			
	25% 104 Glass	A			
	25% Beta Glass	B			
4	25% Lake Asbestos, 25% UC Asbestos	Beaten together for 15 minutes	Fair Formation - Good dispersion of Beta - Some clots of asbestos	100	840
	25% 104 Blass, 25% Beta Glass	Beaten together for 20 minutes			

A Material chopped at 20 gm in 5 liters of H_2O in large Waring Blender at medium setting for 3 minutes.

B. Material chopped at 20 gm in 5 liters of H_2O in large Waring Blender at medium setting for 5 minutes.

C Material beaten in Chest Beater 1 hour, light pressure on bed plate, 20 gm solids in 20 liters of H_2O - (1% consistency).

D Material beaten in Chest Beater 15 minutes, light pressure on bed plate (1% consistency).

formation, provided the long fibers necessary for tear strength. Two types of asbestos were also investigated during the course of the program. A short fiber Chrysotile asbestos available from Union Carbide Corporation (Coalinga) was found to act in a similar manner to the 104 glass fibers as a source of fines. It increased the tensile strength of mixed fiber sheets manufactured from beta glass, 104 glass, and the Coalinga asbestos. A second type of asbestos, Canadian Lake 3T grade, was also investigated because of its long fiber length. Sheets made from this material had higher tear strengths than ones made from the shorter fiber asbestos. However, dispersions of the 3T asbestos were extremely slow draining in the sheet mold and 100% asbestos sheets could not be manufactured in the hand sheet equipment. The addition of the shorter fiber Coalinga asbestos and the 104 glass, greatly improved the sheet drainage rates compared to the Canadian asbestos. A mixture of 25% of 3T asbestos, 25% of Union Carbide asbestos, 25% of Beta glass, and 25% of Code 104 microfiber glass was found to give a free-draining stock which processed into sheets closely resembling cellulosic paper and which had a good balance between tear and tensile strength. This particular blend was given the code name of Dynapaper. Impregnated sheets made from this formula suffered from poor crease resistance and punched through when subjected to the moderate pressure of a ball point pen. They also had poor pick resistance to viscous inks used in the printing process.

4.4 Use of Coalinga Asbestos and 104 Glass as Retention Aids

The 104 glass when dispersed in acidic solutions, possesses a negative surface charge. Coalinga asbestos, when dispersed under similar conditions has a positive charge on the surface of the fibers. When dilute solutions of the two materials are mixed, the particles agglomerate or coflocculate, leading to good retention of the small particles on the forming screen. Beta glass and the two types of clay do not agglomerate to the same extent as do the finer particles of the 104 glass and Coalinga asbestos, leading to poorer retentions on the forming wire when these materials are used alone.

4.5 Beaten Addition of Resins and Their Effect on Sheet Tensile Strength

Generally, two methods are used to impregnate paper sheets with organic resins. One method consists of adding the resin as a "dispersion" or latex directly

to the beater and then coagulating the latex with a substance such as alum. The resin loaded fibers are then made into paper sheets by the conventional paper making processes. This method was used with two resins, Neoprene and the 100 Glass resin, which were of low flammability and which could be made into latexes suitable for beater addition.

The increase in strength with added weight percentages of resin add on is shown in Figure 6. The two points marked "solution polymerization" were samples prepared by the technique used by Vanderbilt (4) to increase the bond strength between fiber glass and rubber. The effectiveness of this technique is quite evident from the higher strengths obtained at the lower % add-ons of latex. Unfortunately, both the OI Glass resin and the Neoprene were flammable and burned at approximately 4-5 in/sec when conventional beater-add techniques were used. A significant reduction in flame propagation rate resulted from the solution polymerization procedure, i.e., for the 40% point the burn rate was reduced from 5" per sec. for the alum coagulated sample to 0.83 in/sec for the solution polymerized sample. Although this was a significant reduction, the basic flammability of neoprene in pure oxygen suggested that other more fire resistant polymers be used as binders.

4.6 Dry Saturation of Sheets With Low Flammability Resins

As an alternative to beater addition of the binder resin, dry saturation of the sheets were investigated. The results of these experiments are given in Table 6. Of the resins investigated, Kynar impregnation of the 50-50 base stock increased the tensile strength 10 fold. As shown in Table 7, impregnation of the stronger Dynapaper only increased the strength approximately 2 fold with little difference in tensile between 7% and 15% addition levels. Since Kynar was found to be flammable at 9-10% weigh % add on, the 7-8% impregnation level was selected for preparation of the sample sheets furnished MSC during the first phase of the contract.

4.7 Scrim Reinforced Sheets

To improve the tear strength of both the margin and the complete sheet of Dynapaper, experiments were performed with glass scrim cloth as a reinforcing core. Sheets of 1/8" square beta glass scrim were fitted over the wire of the sheet

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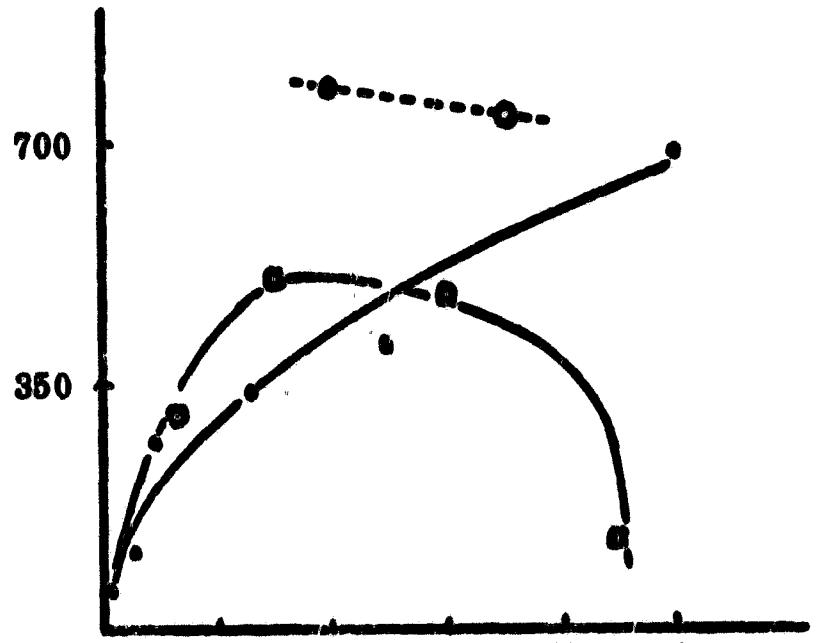
Figure 6



Effect of beater additions of duPont Neoprene Latex 400 and Glass Resin 100 on Tensile Strength of 50% 104 glass, 50% UC Asbestos Sheets

Legend

- ⊙ du Pont 400 Neoprene - solution polymerization*
- ● du Pont 400 Neoprene - alum coagulation
- ◘ Type 100 Glass Resin (Acetone-water-resin emulsion polyphosphate emulsifier)

* Solution polymerization procedure:

Treat glass fibers with A-1100 silane in water solution and then add predispersed asbestos, latex, coagent (difunctional methacrylate), and ammonium persulfate, heat to 180° F and stir gently for one hour.

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Table 6

Dry Saturation of 50% 104 Glass 50% UC Asbestos Sheets

Material	% by Weight Add on resin	Tensile Strength (psi)
Kynar, Scrim, reinforced structure	7.1	4400
Kynar	15.2	1000
CNR Rubber	36	480
CNR Rubber	45	530
O-I 908 Glass Resin	8.3	300
O-I 908 Glass Resin	17.3	370
Teflon	39.0	480
Teflon	52.2	580
Basic Sheet unimpregnated	0	100

Table 7

Dry Saturation of Dynapaper

Material	% by Weight Add on Resin	Tensile psi	Elmendorf Tear grms
Unimpregnated Sheet	0	830	110
Kynar	7.5	1470	50
Kynar heat treated 130°C - 8hrs (pink)	7.2	2200	66
Kynar	13.5	1400	--
Fluorel	27.5	1600	80

mold and the furnish poured over the top. When the foot valve was released a small portion of the fibers filtered through the small openings of the scrim and the remainder formed a sheet on top of the scrim. Although the sheets were quite one sided. the scrim could be buried in the structure and several sheets were made in this manner. An 8.5 mil thick sheet had a tensile strength of 34 lbs/in of width, a tear of 1550 grams and a density of 0.504. Delamination of the paper and scrim was experienced and special equipment to produce this type structure would be required. Also, sheets were prepared with scrim in the margin by laying a piece of scrim in the sheet mold along the left edge of the sheet. The scrim would bow slightly when the furnish was added to the mold and good sheet formation below the scrim could be obtained. A number of sheets with scrim in the margin were prepared in this manner, but delamination and failure at the inboard scrim edge, where the sheet and scrim were joined, indicated that considerable development would be required to make satisfactory sheets, and this approach was not pursued further.

4.8 Flammability Limits of Organic Fiber-Dynapaper Blends

The crease resistance of the basic Dynapaper was improved by additions of other organic fibers. However, without added flame retardants, only PBI and Thornel fibers were self extinguishing when mixed with the basic Dynapaper. Table 8 shows that above 14 % PBI and 14 % Thornel, the blends of Dynapaper and the organic fibers will burn in 16.5 psia pure O_2.

4.9 Flammability Limits for Inorganic Sheets Impregnated With Organic Materials

The stringent requirements for non flammability in 16.5 psia O_2 severely limited the choice of polymers which could be used as binders for the inorganic papers. Candidate materials were tested throughout the course of the contract. The results of the screening tests on various polymers are shown in Table 9. The polymers found to be acceptable and their threshold limits of flammability on the all inorganic paper are listed below.

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Table 8

Flammability of Various Organic-Inorganic Fiber Blends - No Impregnants

% Organic Fiber added to basic Dynapaper formula	Burn Rate - inches/second 16.5 psia O_2	NASA Report No.
8% Dacron	2.5	PLN 2077
20% Dacron	5.0	PLN 2059
2% Cellulose	Failed match test in air	
5% Cellulose	Failed match test in air	
10% Cellulose	Passed match test in air	
100% Cellulose	Flash Fire	PLN 2144
7% PBI	SE 3/4 inch	PLN 2140
14% PBI	SE 1 1/4 inch	PLN 2141
28% PBI	.45	PLN 2142
42% PBI	.38	PLN 2143
7% Thornel	SE 1 inch	PLN 2132
14% Thornel	SE 1/2 inch	PLN 2133
28% Thornel	.55	PLN 2134
42% Thornel	.55	PLN 2135
56% Thornel	.42	PLN 2136

Polymer	Threshold Flammability at 16.5 psia - 100% O_2
CNR	self extinguish at all levels
3203-6 Fluorel	Tested to 40% add on SE in 4 inch at this level
Gayco FR 96-J	SE at 14 % add on
Kynar	SE at 10% add on
PBI Varnish	SE at 7% add on
Viton	28% was SE in 6.2 psia O_2 after heat treatment
OI Glass Resin Type 908	8.3% burned 3.3 inch then SE
Type 100	15% burned 3.5 inch then SE

4.10 Flammability of Miscellaneous Paper Samples

Near the close of the contract, a number of treatments were tried on various substrates to evaluate possible new approaches to the manufacture of a non-flammable paper. These experiments are tabulated in Table 10. The most significant result from these trials is the ability of phosphoric acid salts (diammonium phosphate) either alone or in combination with Fluorel to fireproof cellulose in the 6.2 psia O_2 atmosphere. These promising results were not pursued further due to contract termination. However, further work to optimize the borax-boric acid and phosphoric acid treatments is recommended.

Table 9

Flammability Levels of Various Polymers Impregnated into Non-Flammable Substrates

Polymer Add on Weight	Substrate Description	Flammability in 100% O_2 at 16.5 psia Burn Rate - in/sec	NASA Report No.
Neoprene			
12%	Beater add to 50% 104-50% UC paper	0.4 in. in 4 sec then SE	PLN 1106
25%		5	PLN 1100
50%		5	PLN 1101
40%	Polymerization in solution with 50% 104-50% UC fibers then made into paper	0.83	PLN 1104
O-I Glass Resin			
8.3% type 908	Dry saturation from acetone on 50% 104-50% UC paper	3.3 in/sec then SE	PLN 1311
17.4% type 908		3.3	PLN 1310
15% type 100	Beater addition to 50% 104-50% UC paper	3 1/2 in. in 1 sec then SE	PLN 1103
30% type 100		5	PLN 1107
45% type 100		5	PLN 1102
Kynar			
10%	50% 104-50% UC paper	No ignition	PLN 1159
6.8%	50% 104-50% UC paper	SE	PLN 1299
15%	50% 104-50% UC paper	2.5	PLN 1304
15%	All Beta Glass paper	SE	PLN 1305
CNR			
36%	50% 104-50% UC paper	SE	PLN 1294
45%	50% 104-50% UC paper	SE	PLN 1308
Teflon Dispersion			
39%	50% 104-50% UC paper	3.3	PLN 1306
52%	50% 104-50% UC paper	2.5	PLN 1312
Fluorel L3203-6			
16.6%	Dynapaper	SE tissue; SE silicone igniter	PLN 2195
29.0%	Dynapaper	SE tissue; SE silicone igniter	PLN 2196
34.0%	Dynapaper	SE tissue; SE silicone igniter	PLN 2197
40%	Dynapaper	SE after 4" burn	PLN 2198
20%	10% PBI Dynapaper	SE in 2" 60-40 atmosphere 1.25 in/sec in 16.5-100% O_2	PLN 2295
PBI Varnish (DuPont)			
7%	Dynapaper	4" in 3 sec then SE	PLN 2211
16.1%	Dynapaper	5	PLN 2213
38%	Dynapaper	2.5	PLN 2212
Viton			
28%	10% PBI Dynapaper	1 in/sec 60-40, 16.5 psia; 1.12 in/sec 6.2 100% O_2	PLN 2296
28%	16 hr @ 400°F	0.263 in/sec in 60-40; 16.5 psia. SE in 6.2 psia 100% O_2	
Gayco FR 86 Varnish			
8%	Dynapaper	SE in 2 in	PLN 2070
12.5%	Dynapaper	SE in 4 in	PLN 2071
14%	Dynapaper	SE in 4 in	PLN 2075
*11.8%	Dynapaper	2.5	PLN 2072
20%	Dynapaper	1.66	PLN 2076

* non-uniform coating

Table 10

Flammability of Various Paper Structures with Fire Retardant Treatments

Type of Paper and Description of Dip Coating Solution		Burn Rate - in/sec 16.5 psia 100% O_2	16.5 psia 60% O_2 40% N_2	6.2 psia 100% O_2	NASA Test PLN No.
Nomex Paper					
No coating		not run			
11% Borax-Boric Acid + 11% Fluorel Overcoat				0.4	2458
12% Borax-Boric Acid + 8% Fluorel Overcoat				0.33	2459
20% Borax-Boric Acid + 14% Fluorel Overcoat				0.33	2460
250 Alternate Dip Coats of Alon-C Ludox from Dilute Colloidal Solution		1.33			2055
Dynapaper with Added Fibers					
% Super Added Fiber	% Add on of indicated coating solution				
8% Dacron	No coating	2.5			2077
8% Dacron	≈ 50% Ludox and 8% Gayco solution	1.25			2067
8% Dacron	≈ 50% Aluminum Hydroxide Overcoated 8% Gayco Ludox mix	SE in 2.5			2078
20% Dacron	No coating	5.0			2059
20% Dacron	56% Ludox Overcoated 8.9% Gayco solution	3.33			2058
20% Dacron	23% Clay solution overcoated 4% Gayco solution	3.0			2057
20% Dacron	18% Kynar Overcoated ≈ 20% Ludox-Clay	1.66			2056
30% Dacron	23% Aluminum Hydroxide	2.5			2069
30% Dacron	49% Aluminum Hydroxide overcoated 8% Gayco	1.66			2079
30% Dacron	30 Alternate Dip Coats of Dilute Colloidal solution of Baymal-Ludox	1.66			2080
30% Dacron	No coating - control	not run			

Table 10 (continued)

Type of Paper and Description of Dip Coating Solution Dynapaper with Added Fibers		Burn Rate – in/sec 16.5 psia 100% O_2	16.5 psia 60% O_2 40% N_2	6.2 psia 100% O_2	NASA Test PLN No.
% Super Added Fiber	% Add on of Indicated Coating Solution				
50% Nylon	50% Diammonium Phosphate (DAP)			1.33	2554
50% Nylon	82.5% Diammonium Phosphate			1.0	2553
50% Nylon	23.7% Diammonium Phosphate; 28.4% Fluorel Overcoat			1.0	2552
50% Kraft-Pulp	18.5% DAP; 18% Fluorel Overcoat		SE	SE	2475
50% Kraft-Pulp	56.0% DAP; 17.5% Fluorel Overcoat		SE	SE	2478
50% Bleached Cellulose Pulp	14.5% mix 2:3 DAP, Urea; 14.3% Fluorel Overcoat			2.5	2501
"	12.8% mix 2:3 DAP, Urea; 16.3% Fluorel Overcoat			2.5	2502
"	23% DAP; 25% Fluorel Overcoat			2.0	2549
"	25% DAP; 25% Fluorel Overcoat (hot pressed)			flash fire	2551
"	35.4% DAP; 20.2% Fluorel Overcoat			1.0	2505
"	63.5% DAP; 20% Fluorel Overcoat		SE	SE	2506
"	87% DAP; 18.8% Fluorel Overcoat		SE	SE	2550
100% Dynapaper	49% mix 2:3 DAP Urea; 20% Fluorel Overcoat		SE	SE	2499
100% Dynapaper	51% mix 2:3 DAP Urea; 17.5% Fluorel Overcoat		SE	SE	2500

Table 10 (continued)

Type of Paper and Description of Dip Coating Solution		Burn Rate – in/sec 16.5 psia 100% O_2	16.5 psia 60% O_2 40% N_2	6.2 psia 100% O_2	NASA Test PLN No.
Conventional Cellulose Papers					
Type of Paper	% Add on of Coating				
Vellum – 45 lb	9.1% 7:3 mix Borax, Boric Acid; 17% Fluorel Overcoat			0.8	2464
Vellum	11.1% 7:3 mix Borax, Boric Acid; 15% Fluorel Overcoat			1.0	2463
Vellum	42% DAP; 14.8% Fluorel Overcoat } coating not uniform			2.5	2476
Vellum	60% DAP 22.8% Fluorel Overcoat } coating not uniform			1.6	2477
Vellum	100% THPOH	flash fire			2128
20% Rag Bond	30% DAP; 14.3% Fluorel Overcoat			1.66	2503
20% Rag Bond	31% DAP; 12.5% Fluorel Overcoat			1.66	2504
Waterleaf Blotting Paper	8.5% 7:3 mix Borax, Boric Acid; 7.3% Fluorel Overcoat			0.36	2465
"	8.6% 7:3 mix Borax, Boric Acid (pressed)			0.26	2466
"	36% DAP; 8.1% Fluorel Overcoat		SE	SE	2480
"	38% DAP; 7.5% Fluorel Overcoat			0.02	2479

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