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RESEARCH DIVISION

Washington Research Center, Clarksville, Maryland 21029

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Development of Inorganic Nonflammable Vermiculite Flight Paper

Report of Phase I

by E. W. Lard, Principal Investigator

Covering the Period

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I. Summary

An inorganic paper has been developed from vermiculite plus chrysotile asbestos and Beta glass fibers which is nonflammable in 100% oxygen (16.5 psia), and accepts printing well by the offset process. Although not all properties of this new Vermiculite Flight Paper are equivalent to those of bond paper, nevertheless, the paper has considerable promise for many manned space flight missions.

Best properties obtained to-date are as follows:

Vermiculite Paper	Property	Bond Paper
Off white to light grey	Color	White
6 ± 1	Thickness (mils)	4
>120	Tear Strength(g/sheet)	70
Excellent	Printability by offset	Excellent
~1600	Tensile Strength (psi)	4,000
0.48	Density (g/cc)	0.7
1.78	Weight (oz./yd.^{2})	2.46
9.7	Bursting Strength (lbs./in.width)	15.5
50	Folding Endurance (cycles)	5,000

It is our opinion that Vermiculite Flight Paper can be used in its present form for flight manuals for manned Apollo flights. At the same time, tensile and bursting strengths as well as folding endurance should be improved. To improve these last three properties further is one objective of this continuing program.

Vermiculite Flight Paper has been produced continuously on a pilot Rotoformer paper making machine at the Sandy Hill Paper Co., Hudson Falls, N. Y. Feasibility of producing commercial quantities of this paper has been demonstrated.

To date, over 1,000 sheets of Vermiculite Flight paper have been delivered to NASA/MSC. Most of these have been made on the Sandy Hill Rotoformer.

II. Introduction

Scientists at the W. R. Grace & Co. Research Division first prepared an all inorganic, totally vermiculite paper to replace mica paper for electrical insulations. This paper, called Vemil-120, has the following desirable properties:

- it is completely inorganic and nonflammable
- no toxic gases are evolved when the material is heated
- the surface is smooth and accepts typing and printing
- it is flexible and can be made in thicknesses comparable to that of bond paper
- it has a tensile strength of 1500 psi

On the other hand, Vemil-120 has several disadvantages which made it unacceptable for use in manned space flights. These include:

- low tear strength
- brown in color
- when heated it blisters (due to escape of trapped water)
- the density is double that of bond paper

Vemil-120 is made by exfoliating the raw vermiculite ore with sodium chloride followed by exchanging the sodium cation with lithium. The lithium exchanged vermiculite is ground in water to a fine size, forming a vermiculite dispersion. After adjusting the solids content to about 1%, the dispersion is flocculated by the addition of hydrochloric acid and the flocc is filtered. Because of the non-porous nature of fine size vermiculite platelets, filtration is extremely slow. The finished paper has excellent dielectric properties, but tear strengths of only 5-10 g/sheet.

III. Objectives

Our program was initiated with the clear cut target of improving the tear strength of Vermiculite paper to a value at least as high as that of bond paper, e.g., 70 g/sheet.

Secondly, the improved paper should be capable of being produced on commercial paper making equipment.

Finally, if effort remained, we were to screen the feasibility of making changes in the paper formulation to develop porous paper products such as tissue paper and towels.

IV. Research Program Progress

A. Preparation of Vermiculite Dispersions

Vermiculite ore is mined, ground and washed with detergent and water to remove any organic matter. The washed material is exposed to 1 molar sodium chloride for 24 hours to exchange the Ca and Mg cations for Na ions. Excess sodium chloride is removed by washing with water. This action also exfoliates the mass. The ore is then soaked in 1 molar LiCl overnight to make a lithium dispersion. Excess LiCl is removed by washing and the material is ground through a Manton-Gaulin homogenizer or a Rietz extructor to a very fine size. This dispersion is very homogeneous and does not settle out upon standing.

B. Flocculating Agents for Vermiculite

At the beginning, acids such as hydrochloric and sulfuric were used to cause flocculation. It was reasoned that the smaller ion would allow the platelets to come closer together, thus creating a closer bond and therefore a stronger paper. The first experiments were conducted mostly with hydrochloric acid, however, the flocc was always very fine and was not retained on a 150 mesh screen. It was soon found that calcium and magnesium cations in approximately the same concentration as removed from the original vermiculite ore were the best flocculating agents. A more uniform flocc was obtained when these cations were used in conjunction with sulfuric acid.

C. Laboratory Procedure for Preparing the Paper

Paper was prepared in the lab in a 12 inch diameter Buchner funnel, fitted with a nylon filter cloth. In the beginning, fiber glass was dispersed in one Waring blendor and asbestos in another. The two were combined with vermiculite dispersion and the flocculating agent was added. A nylon filter cloth was placed in a funnel where most of the liquid drained through by gravity. Almost all of the remaining liquid was pulled from the cake by a vacuum. Last traces of water were removed by placing the sheet in an oven at 110°C for approximately 15 minutes.

In the final procedure, approximately one gallon of water containing 3 ml of concentrated H_2SO_4, 1.44 g $Ca(H_2PO_4)_2 \cdot H_2O$, 200 mg $MgCl_2 \cdot 6H_2O$ and 100 mg of LiCl was divided into two portions, 1/8 gal and 7/8 gal. Asbestos (1.5 g) (Plastibest-30; Johns-Manville) was ground in a Waring blendor containing 1/8 gallon of the above for about 3 minutes and then mixed with 0.2 g of Hycar 2671 (acrylate latex-B.F. Goodrich). (50% solution). Fiber glass (1.5 g) (Beta glass; Owens-Corning) was added to the 7/8 gallon of water and stirred for about 20 minutes to disperse the fibers. The two slurries were combined and the vermiculite (50 ml of 5% soln.) was added and thoroughly mixed. The slurry was then filtered and the final sheet dried on a cylindrical dryer.

D. Laboratory Experiments to Increase Paper Strength

As mentioned earlier, the tear strength of Vemil-120 is low - approximately 10 grams/sheet. Therefore, the first objective was to increase this quality of the paper. It is well known that fibers increase the strength of regular paper, therefore, fiber glass and asbestos were evaluated. The first fiber glass to be used was from Owens-Corning M-710 fiber glass mat. This was thoroughly chopped in a Waring blendor, and mixed with asbestos-Ti (Union Carbide). The asbestos is very short fiber chrysotile material coated with TiO_2. This was Sample No. 87 as recorded in Notebook 5249.

Composition	Elmendorf Tear, g.
Vermiculite 80.6%, fiber glass 14.9%, asbestos-Ti 4.5%	20

Since this paper was not strong enough, other types of fiber glass were evaluated. Johns-Manville "Woven Roving" was cut into 1/4 inch lengths ground in a Waring blendor for 15 minutes, mixed with asbestos and vermiculite. This did not produce a stronger paper. Over 100 experiments were conducted to evaluate various flocculating agents and different ways to mix the raw materials.

It was finally decided that the fiber glass should be as long as possible and the Waring blendor was abandoned as a mixing device. Instead, the 1/4 inch "Roving" fiber glass was stirred gently until the fibers were separated. Samples prepared in this manner resulted in paper with tear strengths in excess of 40 grams per sheet as shown in the following test.

Sample No.	Composition (Per Sheet of Paper)	Thickness	Elmendorf Tear
188	5 g. vermiculite;0.3 g. asbestos-Ti; 1.0 g. of 1/4" Roving	0.005"	45 gm

The use of regular tap water instead of distilled water did not change the tear strengths.

The effect of changing asbestos concentration is shown in runs 210-215 as follows:

Paper Containing 5.0 g. Lithium Vermiculite and 1.0 g. 1/4" Fiber Glass (M 710) per Sheet

Code Number	Asbestos (gm)	Average Thickness of Paper (mils)	Tear Strength (gm)	Comments
210*	asbestos-Ti 0.3	3.8	40	Tears too easily
211*	asbestos-Ti 0.3	3.8	37	Pulls apart, not sturdy
212*	asbestos-Ti 0.6	4.0	30	Crumbles easily under handling
213*	Plastibest-30 0.3	3.4	25	No good
214*	Plastibest-30 0.6	3.8	30	No good
215*	Plastibest-30 1.2	6.1	25	No good

*500 mg $CaCl_2$ + 200 mg $MgCl_2 \cdot 6H_2O$ used as flocculating agents.

These results show that increasing the asbestos content (either pure asbestos (Plastibest-30) or asbestos-Ti) beyond a 1-1 ratio reduces the tear strength of the paper. Mr. Sauers, Project officer of NASA, indicated that the feel of paper with TiO_2 was not good, so very few further tests were made with this additive.

In runs 216-218, calcium and magnesium as flocculating agents were varied to determine the best level of these compounds. As indicated immediately below, the lower level (275 mg $CaCl_2$ + 200 mg $MgCl_2 \cdot 6H_2O$) gave the highest tear strength.

Code No.	Vermiculite gm.	Plastibest-30 (gm.)	Fiber Glass Mat 1/4" (gm)	Additives	Average Thickness of Paper (mils)	Tear Strength (gm.)	Comments
216	5.0	1.0	1.0	(using tap H_2O) 275 mg $CaCl_2$ + 200 mg $MgCl_2.6H_2O$	4.1	40	no good
217	5.0	1.0	1.0	(Tap H_2O) 550 mg $CaCl_2$ + 200 mg $MgCl_2.6H_2O$	4.2	25	no good
218	5.0	1.0	1.0	(Tap H_2O) 110 mg $CaCl_2$ + 200 mg $MgCl_2.6H_2O$	4.2	25	no good

Further tests were made with even lower levels of Ca and Mg and with variations in asbestos concentration. The results follow:

225	5.0	0.3	1.0	150 mg $CaCl_2$ + 50 mg $MgCl_2.6H_2O$	4.5	48	doesn't hold up under handling
226	5.0	0.6	1.0	150 mg $CaCl_2$ + 50 mg $MgCl_2.6H_2O$	4.0	48	better (with handling)
227	5.0	0.6	1.0	150 mg $CaCl_2$ + 50 mg $MgCl_2.6H_2O$	5.0	70	no fray-hard to pull apart
228	5.0	0.3	1.0	150 mg $CaCl_2$ + 50 mg $MgCl_2.6H_2O$	4.7	60	weakens with handling

Sample No. 227 (tear strength 70 g.) was sent to NASA for evaluation and was found to be self-extinguishing in 100% oxygen. As indicated, the tear strengths of these sheets are very good, but the fold strengths are poor so various techniques were evaluated to increase this particular property. The fiber glass content was increased with improved tear strength as shown in the table below:

233	5.0	0.6	1.0	150 mg $CaCl_2$ + 50 mg $MgCl_2$	3.8	40	poor tear-weakens with handling
234(226)	6.0	0.6	1.5	150 mg $CaCl_2$ + 50 mg $MgCl_2$ + Tap H_2O	5.3	75	good tear
235(227)	7.5	0.6	1.5	150 mg $CaCl_2$ + 50 mg $MgCl_2$ + Tap H_2O	6.0	90	improved

Code No.	Vermiculite gm.	Plastibest-30 (gm.)	Fiber Glass Mat 1/4" (gm)	Additives	Average Thickness of Paper (mils)	Tear Strength (gm.)	Comments
244	7.5	0.6	1.5	150 mg $CaCl_2$ + 50 mg $MgCl_2 \cdot 6H_2O$+ 150 mg $AlCl_3$	6.0	65	no notable change
246	7.5	0.6	1.5	550 mg $CaCl_2$ + 200 mg $MgCl_2 \cdot 6H_2O$ 150 mg $AlCl_3$	5.7	40	poor
247	7.5	0.6	1.5	360 $Ca(H_2PO_4)_2 \cdot H_2O$+ 50 mg $MgCl_2 \cdot 6H_2O$+ 50 mg $AlCl_3$	6.1	90	good tear
248	7.5	0.6	1.5	1.3 g $Ca(H_2PO_4)_2$+ H_2O + 200 mg $MgCl_2 \cdot 6H_2O$+ 150 mg $AlCl_3$	6.1	70	poor
249	7.5	0.6	1.5	110.7 mg of $Ca(OH)$ + 50 mg $MgCl_2 \cdot 6H_2O$+ 50 mg $AlCl_3$	4.5	65	poor
250	7.5	0.6	1.5	405.9 mg$Ca(OH)_2$+ 250 mg $MgCl_2 \cdot 6H_2O$+ 50 mg $AlCl_3$	6.7	35	poor tear
251	7.5	0.6	1.5	75.0 mg $CaCl_2$ + 25 mg $MgCl_2 \cdot 6H_2O$+ 25 mg $AlCl_3$	6.0	100	good tear
252	7.5	0.6	1.5	75 mg $CaCl_2$ + 25 mg $MgCl_2 \cdot 6H_2O$+ 50 mg $AlCl_3$	6.0	95	good tear

The above experiments indicate that Al^{+3} is a good flocculating agent in conjunction with Ca and Mg, however, the concentration should not exceed 50 mg of $AlCl_3$. It should be noted that $AlCl_3$ alone gives a very small flocc similar to that produced by acids and is very difficult to filter.

Calcium hydroxide was evaluated as a flocculating agent as shown in the following duplicate tests:

251	7.5	0.6	1.5	405.9 mg $Ca(OH)_2$ + 200 mg $MgCl_2.6H_2O$ + 50 mg $AlCl_3$	4.0	67
251	"	"	"	" "	6.2	80
251	"	"	"	" "	6.0	80
251	"	"	"	" "	4.6	75
251	"	"	"	" "	4.6	80

No particular advantage was noted with this composition of flocculating agents

The effect of calcium and magnesium concentration is shown in the following experiments:

295	5.0	1.0	2.0	100 mg LiCl + 275 mg $CaCl_2$ + 100 mg $MgCl_2.6H_2O$	7.7	90
296	5.0	1.0	2.0	100 mg LiCl + 150 mg $CaCl_2$ + 50 mg $MgCl_2.6H_2O$	7.0	85
297	5.0	1.0	2.0	100 mg LiCl + 75 mg $CaCl_2$ + 25 mg $MgCl_2.6H_2O$	6.7	80

As indicated, very little change in tear strength was noted when the $CaCl_2$ and $MgCl_2$ level dropped to 75 and 25 mg respectively/gallon of water. The resulting paper was very thick due to the added fiber glass.

The effect of vermiculite concentration in the paper is demonstrated in the following experiments:

300	0	1.0	2.0	100 mg LiCl + 550 mg $CaCl_2$ + 200 mg $MgCl_2.6H_2O$	3.4	10
301	1.25	1.0	2.0	" " "	4.4	30
302	2.50	1.0	2.0	" " "	5.2	40
303	3.75	1.0	2.0	" " "	5.2	50
304	5.0	1.0	2.0	" " "	5.9	70
305	6.25	1.0	2.0	" " "	6.5	100
306	7.50	1.0	2.0	" " "	7.5	110

Tear strength increases rapidly with additional vermiculite, however, the thickness also increases. From these tests, it appears the vermiculite should not exceed 1.25 g in this composition. The writing quality of this composition is not suitable due to the excess fiber glass.

Since the fold endurance and tear strength still were low, we began studies of organic binders. Hycar 2671, a reactive acrylic latex from Goodrich Chemical Co., was tried first since it was known to absorb onto asbestos. Results of these tests are as follows:

Code No.	Vermiculite (gm)	P[illegible]sti- [illegible]-30 (gm)	Fiber Glass Coated 1/4" (gm)	Additives	Wt. of Paper (gm)	Tear Strength (gm)	Average Thickness (mils)
312	2.5	1.0	2.0	360 mg $Ca(H_2PO_4)_2 \cdot H_2O$ 50 mg $MgCl_2 \cdot 6H_2O$ 100 mg LiCl + 0.5 gm Hycar 2671	5.5	90	5.3
313	2.5	1.0	2.0	360 mg $Ca(H_2PO_4)_2 \cdot H_2O$ 50 mg $MgCl_2 \cdot 6H_2O$ 100 mg LiCl + 0.25 g Hycar 2671	5.3	60	4.6
314	2.5	1.0	2.0	360 mg $Ca(H_2PO_4)_2 \cdot H_2O$ 50 mg MgCl $6H_2O$ + 100 mg Li[illegible] + 0.1 g Hycar 2671	5.3	60	5.5

These experiments show that the tear strength increases when the Hycar concentration is increased. The tear strength for the lowest concentration of Hy[illegible] is about twice the value when no latex is used. It was anticipated that this low level (~3% by wt.) would not seriously affect the non-burning characteristics. Tests conducted at NASA/MSC, Houston, Texas indeed showed that the paper was self extinguishing in 100% oxygen at 16.5 psia. Other additives such as Neoprene Latex 950 and Plaskon (urea-formaldehyde resin-Allied Chemical) were used without a significant improvement over Hycar 2671.

Sample Nos. 5421-318 and 5421-330 were submitted to NASA/MSC in partial fulfillment of this contract. These were chosen to represent typical samples with and without the organic binder (Hycar 2671). Our evaluation of these samples is as follows:

318	5.0	1.0	2.0	550 mg $CaCl_2$ + 200 mg $MgCl_2 \cdot 6H_2O$ + 100 mg LiCl	7.3	50	7.0
318	"	"	"	" " "	7.3	49.	6.2
330	3.0	1.0	2.0	360 mg $Ca(H_2PO_4)_2 \cdot H_2O$+ 50 mg $MgCl_2 \cdot 6H_2O$ + 100 mg LiCl + 0.5 g Hycar 2671	5.2	100	6.6

As can be seen, the sample containing Hycar has twice the tear strength and about one-half the vermiculite.

Evaluation of these samples at NASA/MSC is as follows:

Test	No. 318	No. 330	Bond Paper
Tear strength, grams	90	100	67.8
Breaking strength, lbs	3.0	3.7	12.0
Folding endurance, cycles	6	14	1000
Thickness, inch	0.009	0.0105	0.003
Weight, oz/yd^2	3.26	2.92	2.53
Combustion Rate at 16.5 psi O_2	Self Ext.	Self Ext.	-

It should be noted that sample 330 contained 7.7 wt. % organic binder.

Additional samples were prepared to determine the reproducibility of paper containing 0.1 and 0.25 g of Hycar 2671 as follows:

Code No.	Vermiculite (gm)	Plastibest-30 (gm)	Fiber Glass Coated 1/4" (gm)	Hycar 2671 (gm)	Additives	Wt. of Paper (gm)	Tear Str. (gm)	Average Thickness (mils)	Comments
332	3.0	1.0	2.0	0.1	360 mg $Ca(H_2PO_4)_2 \cdot H_2O$ + 50 mg $MgCl_2 \cdot 6H_2O$ + 100 mg LiCl	5.6	100	6.8	good
335	3.0	1.0	2.0	.25	360 mg $Ca(H_2PO_4)_2 \cdot H_2O$ + 50 mg $MgCl_2 \cdot 6H_2O$ + 100 mg LiCl	5.6	100	6.6	good
337	3.0	1.0	2.0	.25	" " "	5.8	100	6.4	good
338	3.0	1.0	2.0	0.1	" " "	5.5	100	6.2	good
342	3.0	1.0	2.0	0.1	" " "	5.8	100	6.4	good

These results show good reproducibility in weight of final sheet and also in tear strength. It should also be noted that 0.1 g of Hycar was as effective as 0.25 g of the latex.

Additional samples were submitted to NASA as partial fulfillment of this contract. These experiments were made to [illegible] the flame resistance of paper containing two levels of Hycar 2671 [illegible]ulite. Composition and physical data are tabulated below:

378	3.1	1.0	2.0	0.1	360 mg $Ca(H_2PO_4).H_2O$ + 50 mg $MgCl_2.6H_2O$ + 100 mg LiCl	5.5	6.4	100
380	1.5	1.0	2.0	0.15	" " "	4.0	5.4	110

NASA reported that sample no. 380 (3.2% Hycar and 32.3% vermiculite) was self-extinguishing in 16.5 psia of O_2. No. 378 did not ignite. These tests indicate that the level of Hycar is critical and probably should not exceed 3.5% when the vermiculite concentration is 1.5 g/sheet or less.

Mr. Sauers of NASA indicated that Kynar (vinylidene fluoride resin by Pennsalt) is an effective non-burning binder for asbestos and fiber glass. Samples were made with this binder and compared with paper containing Hycar 2671. The data are recorded below:

Code No.	Ver. (gm)	Asb. (gm)	F.G. (gm)	Hy-car (gm) 2671	Ky-nar (gm)	Additives	Wt. of Pap-er (gm)	Aver-age Thick-ness (mils)	Tear Strength
388	1.0	1.0	1.0	0.1	-	360 mg $Ca(H_2PO_4)_2.H_2O$+ 50 mg $MgCl_2.6H_2O$ + 100 mg LiCl	3.9	6.1	90
391	1.0	1.0	2.0	-	0.5	" " " "	3.9	6.1	50

These samples show that Kynar is not nearly as effective as Hycar, even when the concentration of fiber glass is approximately twice the level with the Kynar. Both of these samples were reported to be non-burning by personnel at NASA/MSC.

Fiber glass used in all the above tests was of the stiff variety that irritates the skin and, therefore, was not acceptable to personnel at NASA/MSC. Mr. Sauers suggested the use of Beta fibers, a new development by Owens-Corning. This material is very soft and does not irritate the skin. A sample of the material in 1/4 inch length was requested, and used for the remainder of the program. Personnel of Owens-Corning (Ashton, R.I. labs), developed a process for dispersing the fibers which included a treatment with NH_4OH and H_2SO_4. We found that the fibers could be readily separated with a solution containing 1.44 g. of $Ca(H_2PO_4)_2$ and 2 ml of concentrated H_2SO_4/gal. The use of Ca in this form as the flocculating was better than as $CaCl_2$. Several sheets of paper were made with Beta fiber glass as detailed in the following:

					Composition				
Code No.	Ver. (gm)	Asbestos (gm)	Fiber Glass (gm)	LiCl mg.	$Ca(H_2PO_4)_2 \cdot H_2O$ $MgCl_2 \cdot 6H_2O$ mg.	Hycar (gm)	Wt. of Paper (gm)	Average Thickness (mils)	Tear Strength (gm)
413	1.0	0.5	2.0	100	360 + 50	0.1	-	5.2	160
414	1.0	0.5	1.0	100	" "	"	-	2.8	100
415	1.5	0.5	2.0	100	" "	"	-	4.9	110
416	1.0	0.5	1.5	100	" "	"	-	3.9	80
419	1.5	0.5	1.0	100	" "	"	-	2.2	50
420	1.5	0.5	1.5	100	" "	"	-	3.1	100
421	2.5	0.5	1.0	100	" "	0.2	3.6	3.8	110
422	2.5	0.5	0.5	100	" "	0.2	3.0	2.6	40

Many of these samples had very good tear strength but did not have acceptable writing surfaces.

Paper with acceptable writing surface was prepared in the laboratory using the following formula:

1.5 g. Beta fiber glass, 1.0 g Plastibest-30 Asbestos,
1.0 g. lithium vermiculite, 0.1 g. Hycar 2671 latex

The big difference between this formulation and those above was the addition of NH_4OH to neutralize the H_2SO_4 and to produce $(NH_4)_2SO_4$ to fix the Hycar latex.

Two hundred sheets of this formulation were made in the laboratory and sent to NASA, Houston for evaluation. Our tests showed the following:

Sample No.	Composition	Thickness Mils	Density g/cc	Wt. Oz.Yd.^{2}	Tear Str. gm	Tensile Strength psi.
5421-472 Lab Sheets	Li Vermiculite = 27.8% Beta Fiberglas ¼"=41.7% Asbestos,Plastibest 30= 27.8% Hycar 2671 = 2.7%	4.42	0.48	1.35	84	1599

These sheets were successfully printed in an off-set press at the W. R. Grace Research Division.

V. Development Program Progress

Having progressed satisfactorily in the laboratory, the next step was to make paper on equipment approximating commercial paper making equipment. Pre-contract discussions with various paper consultants had narrowed down the possibilities to a Rotoformer. The Sandy Hill Paper Co., Hudson Falls, N. Y. is in the business of designing Rotoformers for various specialty papers. In addition, Sandy Hill Paper Co. has a pilot unit capable of producing 8" wide paper continuously. This pilot unit is available on a rental basis.

We chose to rent this machine at Sandy Hill because it closely approximates a larger Rotoformer unit (26 inches wide) owned by the Grace Dewey & Almy Division and located at Cambridge, Mass. In the event that large quantities of paper are required, scale-up from the Sandy Hill 8" wide pilot unit to D&A's 26" wide semi-works unit should offer the least technically complicated route.

A. Preparation of Lithium Vermiculite

The following procedure was used for making dispersion from # 3 vermiculite ore.

1. 50 gallons of water were added to a 100 gallon glass-lined reactor and boiled for about 2 hours and the contents discharged.

2. The reactor was then charged with 50 gallons of fresh tap water, 60 lbs. of raw vermiculite ore and 30 grams of Ultrawet D.S. The slurry was agitated for 2 hours, discharged into polyethylene lined drums and washed thoroughly with tap water.

3. The ore was recharged to the reactor, then 15 lbs. of sodium chloride and 25 gallons of tap water were added. The contents were refluxed for two hours and then discharged into polyethylene lined drums and washed thoroughly with tap water.

4. The solids were recharged to the reactor and 25 gallons of deionized water were added along with 25 lbs. of lithium chloride and the contents refluxed for 4 hours then discharged into polyethylene lined drums. The solids were washed with deionized water three times.

5. The volume was adjusted to 70 gallons by adding deionized water then the slurry was passed through a Rietz Extructor. The dispersion was collected in 55 gallon polyethylene lined drums for future use. A flow diagram is included as Exhibit I.

B. Continuous Production of Vermiculite Paper

Our first trip to Sandy Hill Paper Co. was made on April 10, 1968 to determine if a Rotoformer could be used to produce a wet sheet from 80% lithium vermiculite, 15% fiber glass (1/4" Roving) and 5% asbestos. The Rotoformer is a special machine developed by Sandy Hill and consists of a cylinder about 5 feet in diameter and 1 foot wide. The cylinder is so constructed that the 1 foot width is covered with a wire screen. In operation, the cylinder turns through the slurry where a thin film is deposited on the wire screen with the aid of vacuum. There are four sources of vacuum on the Rotoformer to aid in continued removal of water from the wet sheet.

After several attempts, a few feet of paper were produced from small portions of slurry. Then 400 gallons of slurry were prepared and about two hundred feet of paper was made. Several feet of this paper were sent to NASA, Houston to show that the process was feasible. This paper was light brown in color, had poor tear strength (about 20 grams/sheet), and was porous.

One very interesting discovery resulted from this plant run - it was found that the tap water at Sandy Hill had enough Ca and Mg to flocc the vermiculite. Analysis of the water showed a hardness of 160 ppm as $CaCO_3$; the magnesium content as $MgCO_3$ was 23 ppm.

Work continued in the lab to develop the best formulation for other pilot runs scheduled near the end of the initial contract period. Three days (May 27-29, 1968) were used to produce the paper from vermiculite, asbestos and fiber glass. In the first run, 1/4 inch Roving (Johns-Manville) was used, but the material stuck to the dryer and caused glass fibers to be dispersed upon removal from the dryer with a scraper. All subsequent runs were made with Beta fiber glass (Owens-Corning). The Rotoformer was covered with 20 and 70 mesh screens in that order. In general, the equipment was operated as follows:

Rotoformer 1st box - 10 inches Hg vacuum
Rotoformer 2nd box - 12 inches Hg vacuum
Rotoformer 3rd box - 12 inches Hg vacuum
Suction pick-up roll - 10 inches Hg vacuum
Pressure over the pick-up roll - 15 psig
Dryer temperature - 180°F
Production speed - 7-15 ft./min.

In a typical run, 100 gallons of water and 400 grams of Plastibest-30 asbestos (Johns-Manville) were charged to the 450 gal. mix tank and the mixture was passed through a beater (grinder) to obtain a uniform size. This slurry was pumped out into a separate container where the 80 grams of Hycar 2671 (acrylic latex) was added with vigorous mixing. Three hundred (300) gallons of water, 800 ml. of concentrated H_2SO_4, 40 grams of LiCl and 400 grams of Beta fiber glass were added and this mixture stirred vigorously for 20 minutes. Then the asbestos-Hycar mixture and 20 liters of 10% lithium vermiculite dispersion were added and mildly mixed to prevent foaming. This mixture produced a very uniform flocc.

The normal operation of this pilot plant is such that the slurry is fed to a hold tank and then pumped up to the vessel for feeding the Rotoformer. During the first plant run, it was noticed that the flocc had been destroyed by the time it reached the Rotoformer screen and most of the vermiculite and asbestos was lost through the screen. We found that the high speed <u>centrifugal</u> pumps (1700 rpm) were responsible for this and by-passed them. The slurry was carried by bucket from the hold tank to the make-up system for the Rotoformer and a good sheet was laid down on the screen. Several runs were made to determine the optimum concentration of solids at the Rotoformer. All paper produced during these runs (7) was of poor quality (low tear strength).

Using the experience from the May runs and additional information gleaned from lab studies, we returned to the pilot plant on June 6 and 7, 1968.

After solving several mechanical problems and covering the dryer with cotton broadcloth, several hundred feet of paper were produced from the following formulation:

400 gallons H_2O
500 g. Beta fiber glass
750 g. Plastibest-30 asbestos
150 g. Hycar 2671 (dry solids basis)
500 g. vermiculite (as lithium vermiculite dispersion)

Personnel at Sandy Hill Corp. had installed a 100 mesh screen over the 70 mesh screen just prior to this run.

Five-hundred sheets of this material were sent to NASA, Houston, however, the tear strength (about 50 grams/sheet) was not strong enough for the intended use.

We obtained a three-week extension to continue the project and returned to Sandy Hill on June 25 and 26, 1968 to determine why the paper produced in the plant was not as strong as that made in the lab (lab paper has tear strengths in excess of 100 grams/sheet).

Studies in the lab showed that better paper could be produced from a composition slightly different from that used in the early June pilot plant run. It was also reasoned that additional calcium and magnesium would produce a harder flocc and thus reduce the problems in the wet end of the process. Three runs were made at standard operating conditions with the following formula:

400 gals. H_2O	30 g. LiCl
1250 g. Beta fiber glass	7.5 g. $MgCl_2 \cdot 6H_2O$
1000 g. Li vermiculite	600 ml H_2SO_4
1000 g. Plastibest-30 asbestos	600 ml NH_4OH
225 g. $Ca(H_2PO_4)_2 \cdot H_2O$	105 g. Hycar 2671

In these runs, the 1000 g. of asbestos was ground in a beater and the slurry (100 gals.) removed. Three-hundred gallons of water, 600 ml. H_2SO_4, 225 g. $Ca(H_2PO_4)_2 \cdot H_2O$, 30 g. LiCl, 7.5 g. $MgCl_2 \cdot 6H_2O$ and 1250 g. of Beta fiber glass were added, and mixed for 20 minutes to disperse the individual fibers. The asbestos slurry was added and mixed, then the Hycar 2671 (diluted to 1 gal) was added under mild agitation and the mixture was allowed to stand for 5 minutes. The vermiculite (10 l.) was diluted with 10 l. of deionized H_2O and added with mild agitation. Concentrated NH_4OH (600 ml.) was added to fix the latex resin and completely collapse the vermiculite platelets over the fibers. This did produce a hard flocc that could be pumped into the make-up tank for the Rotoformer.

Our attention then was focused on the drying end of the process. Here we found that the pressure roll on the dryer was breaking the fibers causing the paper to be weak. Pressure on the vacuum roll also reduced the strength of the final sheet. Pressure was removed at both points and the wet sheet was taken up to the dryer by another felt that held the sheet in place while drying. Paper produced in this manner was strong (>100 g. tear strength) but the surface was not smooth. A "dandy" roll was placed on the Rotoformer screen just at the water level. This helped to smooth out the bumps. Several hundred feet of paper were produced, however, the edges on the 8 inch screen were plugged and only 7 inch paper could be made. Laboratory tests on this paper showed the following results:

color - light grey	tear - 120 g/sheet
thickness - 5 mils	printability - excellent
folding endurance - ~40	tensile strength - 1600 psi
weight - 1.78 oz./yd.^{2}	density - 0.48 g./cc.

On July 11-12, 1968, over 500 feet of 8" paper was produced at the Sandy Hill pilot plant using the formula and operating conditions as described above.

Five-hundred sheets 8 x 11" from the plant run were mailed to the Transportation Officer, NASA, along with 200 sheets 8 1/2 x 11" that were produced in the lab.

VI. Conclusions

A. A nonflammable paper has been developed which is self-extinguishing in 100% oxygen at 16.5 psia. The paper has high tear strength (nearly double that of bond paper) and is readily printed by the offset process.

B. In comparing the properties of vermiculite paper with those of bond paper at the present state of development, vermiculite paper has lower tensile strength and folding endurance. Additionally, vermiculite paper is off-white to light grey in color.

C. Vermiculite paper is made by proper blending of Beta-glass fibers (which confer high tear strength), chrysotile asbestos (which allows rapid filtration of the pulp) with chemically exfoliated vermiculite dispersions (which provides smooth surfaces that accept ink).

D. Over 1,000 feet of paper 8 inches wide have been made on pilot paper making equipment. The process appears to be a practical one for further scale-up.

VII. Remaining Problem Areas

Although pilot quantities of vermiculite have been made by a commercially practical process, there are still some refinements to be made. There are no problems remaining with combining of ingredients to form a pulp or forming the wet sheet. However, drying still is a problem, mainly because we have not had the time to try many of the different types of paper drying equipment. Surface characteristics of the finished paper will be affected by varying the drying technique, e.g., rate of heating, temperature, pressure, etc. and sufficient experimentation must be conducted to firm the proper dryer and its use.

Additionally, the current process should be scaled-up from 8" wide to 26" wide paper to (a) produce larger quantities (thousands of sheets/day) of paper, and (b) allow costs to be defined.

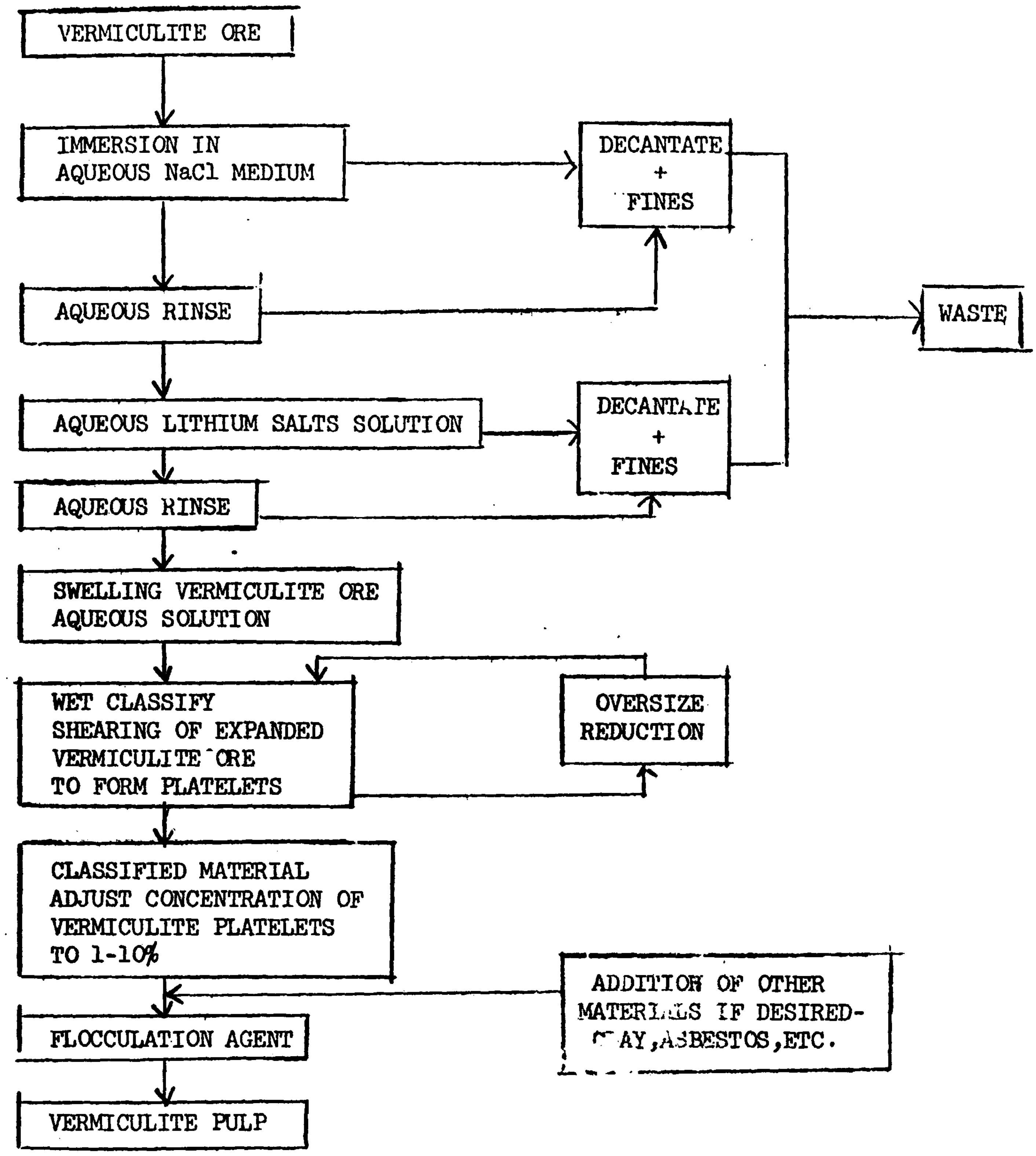
Further, major improvements in paper properties, such as tensile strength, folding endurance and color can be achieved, but will require more sophisticated chemistry than has been applied thus far to the system. Efforts are being made to find a water dispersible, nonflammable binder which will allow the use of greater amounts thus increasing tensile strength and folding endurance.

Surface treatment with GACO (a fluorinated hydrocarbon) after forming the paper has resulted in vastly improved printability. Incorporation of fine size white pigments into GACO should mask the off-white or grey color.

Removal of iron (which is responsible for most of the color of vermiculite) by selective chelation is a promising, but sophisticated, method of attacking the color problem.

To produce porous papers capable of absorbing large quantities of water, for use as tissue, toilet or toweling paper, major revision of the basic formulation will be required. For such purposes, wet strength will be the key physical property and glass fibers must be eliminated (because of irritation to human skin).

EXHIBIT I



VERMICULITE ORE
IMMERSION IN AQUEOUS NaCl MEDIUM
DECANTATE + FINES
AQUEOUS RINSE
WASTE
AQUEOUS LITHIUM SALTS SOLUTION
DECANTATE + FINES
AQUEOUS RINSE
SWELLING VERMICULITE ORE AQUEOUS SOLUTION
WET CLASSIFY SHEARING OF EXPANDED VERMICULITE ORE TO FORM PLATELETS
OVERSIZE REDUCTION
CLASSIFIED MATERIAL ADJUST CONCENTRATION OF VERMICULITE PLATELETS TO 1-10%
ADDITION OF OTHER
FLOCCULATION AGENT
VERMICULITE PULP