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STATUS REPORT

NEW ENTERPRISES
CHEMICAL REACTIONS OF ASBESTOS

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Date: November 2, 1964

Project No.: 162D21

File No.: 3180

SUMMARY The addition of acrylic acid to asbestos was studied to determine the feasibility of producing an acrylate modified asbestos surface reactive in vinyl polymerization reactions. Under aqueous conditions reasonable organic loadings could only be achieved after long reaction time. Under anhydrous conditions organic loading was chiefly due to precipitation of polyacrylic acid.

The modified asbestos rapidly lost organic material in water due to facile hydrolysis. Samples of treated asbestos were tested for cross-linking ability in a vinyl cured polyester. An average of 37,000 psi in flexural strength was noted for polyester specimens filled with treated asbestos vs. an average of 11,000 psi for polyester controls filled with raw asbestos. Flexural modulus, compressive modulus, and modulus of elasticity were all significantly higher for polyesters filled with treated asbestos, indicating that vinyl cross-linking did take place.

Anion exchange was considered as an alternate means of introducing carboxylate ions to asbestos but was found ineffective for acetate ion and the idea was abandoned.

Asbestos adsorption of magnesium ε-hydroxycaproate was found to be quite weak and unsuitable as a means of placing organic hydroxyl groups on the asbestos surface.

No further work on organic modification of chrysotile is planned.

INTRODUCTION The reaction of carboxylic acids with asbestos results in a combination of magnesium extraction and carboxylate ion replacement of hydroxide ions on the asbestos surface.(1) This reaction has been investigated as a means of attaching reactive organic functional groups, especially vinyl and hydroxyl groups, to asbestos.

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Other potentially useful methods of placing a carboxylate ion surface on asbestos are ion exchange and asbestos adsorption of magnesium carboxylate salts.

Ethylene-acrylic acid copolymers have been reported to cross-link with chrysotile.[3] The modification of the asbestos surface with a reactive monomer theoretically could convert asbestos to a reactive polymer which might be cross-linked if it could be chemically combined in an organic polymerization system. Such chemical incorporation of asbestos as a reactive filler should result in improved strength properties over conventional filled resins due to an effective increase in molecular size.

DISCUSSION Asbestos was allowed to react with acrylic acid in water and in toluene (Table I). Under aqueous conditions both addition and magnesium extraction took place with magnesium extraction predominating at low acid concentration and addition more prominent at higher acid concentration. This is just the opposite of the results found with acetic acid by Smith and Shriver,[1] and is due in part to polymerization of acrylic acid at higher concentration and precipitation of some of the polymer on asbestos. This is evident from unsaturation determinations carried out on the modified asbestos and partial extraction of polyacrylic acid in dimethyl formamide.

When the reaction was run under non-aqueous conditions magnesium extraction was practically nil. At higher concentrations the organic uptake was much faster than that reported for asbestos and acetic acid by Smith and Shriver,[1] and was predominantly polyacrylic acid which is insoluble in the solvent employed, toluene. Organic loadings at low acid concentration were too low and the reaction rate too slow for practical application.

Two types of addition occurred. An infrared spectrum of the reaction product dried at 105° for 3 days showed the presence of both carboxyl groups and carboxylate ions. Immediate washing of the reaction product with heptane resulted in the extraction of only small amounts of acrylic acid approximating the concentration of acrylic acid in the residual reaction solution wetting the product. On drying at 105°, the product showed a rapid weight loss due to solvent for about one day and then a slow but continuous loss of weight over a period of two weeks. Unsaturation values did not decrease with drying time. A mixture of acrylic and polyacrylic acids could be extracted with boiling dimethylformamide. The residual acids on asbestos then contained a higher proportion of

vinyl groups than before extraction. Therefore, addition of carboxylic acids to asbestos occurs by both chemical reaction and physical adsorption; physical adsorption is more effective in the addition of polyacrylic acid than for acrylic acid due to relative solubility and acidity. Physical adsorption of polyacrylic acid is much less noticeable in the aqueous reaction due to the solubility of poly-acrylic acid.

The products of acrylic acid reaction with asbestos were white powders resembling asbestos, but of greatly reduced bulk and increased cohesion. The products were hydrolytically unstable; on standing overnight in water, samples lost all organic material.

As a determination of the cross-linking ability of acrylate-modified asbestos, two product samples and a pure chrysotile control were milled with varying amounts of MFG 3482 polyester resin and compression molded. The strength properties of the moldings are summarized in Table II.

There are no significant differences in tensile strength between cured polyester samples filled with raw chrysotile and those filled with acrylate modified chrysotile but elasticity decreases and modulus of elasticity increases with acrylate loading on asbestos.

The polyester specimens filled with treated asbestos show a definite increase in compressive strength over those filled with raw asbestos and compressive modulus is markedly increased.

In flexural properties, the increase in strength with acrylate loading on asbestos is striking. With low acrylate loading, 0.29 equivalents of acrylate ion per formula weight of asbestos (3GWR120), little change over polyester filled with untreated asbestos is noted, but with higher acrylate ion loading, 1.72 equivalents of acrylate ion per formula weight of asbestos (3GWR106-1), flexural strength of filled polyester is almost four times that of samples containing untreated asbestos and flexural modulus is increased by as much as a factor of ten.

This evidence strongly indicates that cross-linking has occurred by vinyl copolymerization of the polyester components with adsorbed acrylate ion.

Acrylate-modified asbestos should be patentable as a composition of matter and a memorandum is being prepared to cover the modification of asbestos with unsaturated carboxylic acids as well as vinyl polymers derived from such systems. The products may be useful in applications demanding very rigid plastic materials.

As an alternate method of attaching carboxylate ions to asbestos, exchange of acetate ions for hydroxide ions was attempted. Downward flow of a sodium acetate solution through a column of chrysotile was impossible due to packing so a slurry of 30 g. of chrysotile in 500 ml. of 6 N sodium acetate was stirred at 108° for a period of 100 hours. Immediate potentiometric titration of the supernatant solution indicated only acetate ions and no measurable hydroxide ion concentration.

The asbestos carboxylate surface could be merely due to adsorbed magnesium carboxylate. To test this hypothesis asbestos was stirred with a hot solution of magnesium ϵ-hydroxycaproate. When the product was merely filtered and dried the ashing weight loss was 56%. When the product was washed with cold water and dried the ashing weight loss was 15%, indicating no remaining organic material. The unwashed product was a plastic adhesive mass which lathered much like "Lava" soap.

CONCLUSIONS The reaction of carboxylic acids with asbestos results in an asbestos surface modified by both carboxylate ions and physically adsorbed carboxylic acid.

The reaction products are very unstable to hydrolysis.

While direct reaction of aqueous carboxylic acids could be used to attach substituted carboxylic acids to asbestos, the reaction is probably too slow for practical purposes.

Under anhydrous conditions, carboxylic acids are also slow to add to asbestos unless polymerization is possible, allowing precipitation of a polycarboxylic acid. High loadings of acrylic acid on asbestos occur chiefly by precipitation as polyacrylic acid.

Precipitation of magnesium carboxylate salts on asbestos does not result in a stable product.

Unfavorable equilibrium rules out anion exchange as a means of introducing carboxylate ions to asbestos.

Cross-linking of vinyl polymerized polyester with acrylated modified asbestos appears to occur as evidenced by a fourfold icrease in flexural strength in a polyester filled with treated asbestos over an asbestos filled control.

EXPERIMENTAL

Reaction of Acrylic Acid With Asbestos

Solvent, acrylic acid, and inhibitor were placed in a round bottom flash equipped with stirrer, thermometer, and reflux condensor. The asbestos was added in small portions with stirring to achieve maximum dispersion and the reaction was heated to the desired temperature. Heating and stirring were continued and samples were pulled at the desired intervals. Unless noted, all samples were immediately filtered and dried at 105°C. See Table I for details.

Determination of Organic Content of the Treated Asbestos

The weight loss on ashing of the dried samples was determined as reported previously.(2)

Determination of Unsaturation

The general procedure followed is that outlined in the Union Carbide Chemicals Division Laboratory Manual, General Methods of Analysis 31-10A1-9.

(1) Weighed samples were placed in three tared 250 ml. glass-stoppered Erlenmeyer flasks. Sample size was determined by the formula:

$$\text{Sample Wt.} = \frac{0.072 \times 0.126 \times 100}{\%\ \text{organic material}}$$

(3) 50 ml. of 0.2 N bromine-sodium bromide reagent was pipetted into each flask and allowed to stand 1.5 hours.

(3) 100 ml. of methanol and 10 ml. of saturated potassium iodide solution was added.

(4) The slurry was then titrated with standard 0.1 N sodium thiosulfate to a starch end point.

$$\%\ \text{Theor. Unsat.} = \frac{5(B-A)N \times 72.07}{\%\ \text{organic} \times \text{sample wt. (in g.)}}$$

A = ml. of N normal sodium thiosulfate for sample
B = ml. of N normal sodium thiosulfate for blank

Results were internally consistent ± 3%.

Ref: 3GWR116

July 10, 1964

Attempted Exchange of Acetate Ions For Hydroxide Ions on Asbestos

A slurry of 30.0 g. of Coalinga Chrysotile in 500 ml. of distilled water containing 246 g. of sodium acetate (6M) was heated to 108°C. and stirred at that temperature for 100 hours. The slurry was filtered rapidly while hot and a 50 ml. sample of the filtrate was titrated potentiometrically with 3 N hydrochloric acid. The titration plot described a smooth curve with a break at the acetate end point.

Reference: 4GWR18 August 18, 1964

Addition of Magnesium ε-Hydroxycaproate to Asbestos

To a warm solution of 343 g. of sodium hydroxide in one liter of distilled water was added dropwise 1103 g. of ε-caprolactone. After the exotherm had subsided, a solution of 847 g. of magnesium chloride in 667 ml. of distilled water was added with stirring. The solution was heated to 100° and 100 g. of CMS grade chrysotile was added in 10 g. portions. Heating and stirring were continued for 10 hours, and the solution was filtered hot. Approximately half of the filter cake was immediately placed in a drying oven at 105° and dried for 3 days. On ashing at 900°C. the weight loss was 56%.

The remaining half of the filter cake was washed with three 100 ml. portions of cold water and then dried as above. The weight loss on ashing was 14.5%.

Reference: 4GWR12 August 12, 1964

Molding of MFG Polyester 3482 With Treated Asbestos

The filler material and polyester were weighed in the proportions indicated in Table II to obtain a total weight of 50.0 g. One per cent of benzoyl peroxide initiator was added to the polyester which was then milled cold with the filler material on a 3 x 8 inch roll mill for five minutes. The charge was transferred to a 5-1/4 inch compression mold, taken to 30 tons pressure, and heated to 120°. All specimens were treated in the same way except samples 3GWR130-10 and 3GWR130-11 which were molded at a total pressure of 15 tons.

Filler Materials

3GWR120

11.1% organic material, 30.4% unsaturated
0.29 equivalents acrylic acid/F. W. Asbestos (554.2 g.)

3GWR106-1

18.3% organic material, 100% unsaturated
1.72 equivalents acrylic acid/F. W. Asbestos (554.2 g.)

CMS Coalinga Chrysotile

Dried at 105° for 48 hours
Less than 1% organic material

Reference: 3GWR130 July 27, 1964

REFERENCES

(1) C. W. McGary, P. L. Smith, and L. C. Shriver, "New Enterprises: Asbestos Reinforced Resins", Status Report, October 7, 1963, File No. 1342.

(2) C. W. McGary and G. W. Rausch, "New Enterprises, Chemical Reactions of Asbestos", Status Report, July 16, 1964, File No. 2819.

(3) Hendricks, Imhof, Merriam, and Stenstrom, Memorandum Report; New Resins Evaluation, October 31, 1963, Research and Development Department, Union Carbide Plastics Division.

ATTACHMENTS: 2 Tables

Gerald Rausch

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Union Carbide trial exhibit Union Carbide 85: Union Carbide Research Status Reports on Chemical Reactions of As...
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TABLE I

Sample Number	Wt. Asbestos	Wt. Acid	Solvent	Volume Solvent	Temp.	Time	Inhibitor	% Inhibitor	Drying Time (Days)	% Organic	Unsaturation % Theory	Comments
3GWR90-1	30.0	24.6	H_2O	700	99	4.5	hydroquinone	1.0	4	3.4		
3GWR90-2	30.0					8			4	3.7		Product extracted w. heptane
3GWR90-3	30.0					12			4	6.0	100	Product extracted w. heptane
3GWR96-1						1			1	17.6		Product extracted w. heptane
									15	15.9		
3GWR96-2						2			18	14.9		
									25	14.1		
3GWR96-3						3			1	20.5		
									15	16.4		
									18	15.5		
3GWR96-4						6			25	14.6		
									1	20.6		
									7	18.0		
3GWR96-5						10			11	16.3		
									15	16.2		
									18	15.1		
3GWR96-6						16			25	13.7		
									3	22.2		
									14	20.0		
3GWR96-7						24			17	18.2		
									24	17.0		
									3	22.8		
3GWR104-1	107	268.5	H_2O	2550	100°	3	hydroquinone	1.0	10	20.1		
3GWR104-2	24	60.2	H_2O	500	100°	3	hydroquinone	1.0	14	19.0		
3GWR106-1	120	602	H_2O	2550	100°	3	hydroquinone	1.0	17	19.0		
3GWR106-2	24	120	H_2O	500	100°	3	hydroquinone	1.0	1	28.3		
3GWR108-1	150	126	Toluene	3375	110°	0	MMHQ (.012 ppm)	--	2	27.5		
3GWR108-2						3			6	24.6		
3GWR108-3									10	23.8		
						6			13	24.0		
3GWR108-4						9			21	21.4		
									1	29.2		
3GWR108-5						13			2	28.3		
									6	25.8		
3GWR108-6						18			10	24.9		
									13	24.9		
3GWR112-2	150	1260	Toluene	2240	115°	3			21	24.0	50	
									8	1.3		Workup after 24 hr. standing
3GWR112-3						6			10	15.6	98%	Immediate workup
									14	16.2	100	Workup after 24 hr. standing
3GWR112-4						9			10	14.3	100	Immediate workup
									1	2.2		
3GWR112-5						13			1	3.7		
									13	2.1		
3GWR112-6						18			4	4.6		
									12	3.2		
									4	5.3		
3GWR120	150	1260	Toluene	2240	110	10	hydroquinone	1.0	12	4.2		
3GWR123	150	1260	Toluene	2240	110	10	hydroquinone	0.25	1	7.1		
3GWR125	150	1260	Toluene	2240	110	10	hydroquinone	0.05	2	6.3		
3GWR127	150	1260	Toluene	2240	110	10	hydroquinone	2.0	8	4.5		
3GWR132	150	1260	Toluene	2240	110	14	2,5-diphenyl-p-benzoquinone	0.1	1	9.2		
									2	8.7		
3GWR135	150	1260	Toluene	2240	110	14	2,5-diphenyl-p-benzoquinone	0.1	8	6.9	90	
									1	15.9		
4GWR1	150	126	Toluene	3375	110	20	2,5-diphenyl-p-benzoquinone	0.1	13	7.8		
									15	7.7		
4GWR4	150	630	Toluene	2870	110	18	2,5-diphenyl-p-benzoquinone	0.1	4	20.9		
									11	11.6		
4GWR8	150	1260	Toluene	2240	110	18	2,5-diphenyl-p-benzoquinone	0.1	15	12.6		
									4	20.9		
									11	16.9		
									15	16.6		
									1	38.7		
									2	32.6		
									7	19.8		
									11	19.0		
									1	31.7		
									2	29.1		
									7	26.5	9.0	
									11	25.3		
									3	11.2	30	
									3	10.8	28	
									3	9.5	21	
									3	12.7	25	
									3	8.9	24	Stirrer stopped - Hot spots?
									3	13.5	29	
									3	4.0	100	
									3	9.0	28	
									3	22.2	17	

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TABLE II

Reference	Resin/Filler		Filler	Tensile Properties			Flexural Properties*		Compressive Properties*		Sample Thickness(4)
				Tensile Strength(1)	% Elongation	Modulus of Elasticity(2)	Flexural Strength(1)	Flexural Modulus(2)	Compressive Strength(1)	Compressive Modulus(3)	
3GWR130-3	50	50	Asbestos	3950	1.8	3.86	9,000	7.96	16,900	2.31	.056
3GWR130-2			3GWR120	6475	2.7	3.70	12,290	7.14	27,480	2.52	.058
4GWR16-1			3GWR106-1	4620	1.1	7.5	33,940	78.8	24,950	7.55	0.67
3GWR130-5	45	55	Asbestos	6560	2.1	4.35	10,950	10.5	19,540	2.96	.068
3GWR130-4			3GWR120	7800	5.9	3.33	13,090	7.49	27,600	2.78	.069
3GWR130-7	40	60	Asbestos	6680	3.4	3.80	10,430	6.20	20,370	2.64	.073
3GWR130-6			3GWR120	7485	2.8	3.61	12,360	5.99	23,880	2.59	.075
4GWR16-3			3GWR10601	5290	1.3	7.80	44,430	41.2	24,450	7.17	.086
3GWR130-9	35	65	Asbestos	8525	2.4	4.50	14,360	10.0	26,350	2.94	.087
3GWR130-8			3GWR120	6550	3.3	3.18	12,270	7.04	23,730	2.83	.090
4GWR16-4			3GWR106-1	5115	1.0	6.63	43,090	43.9	24,280	7.10	.097
3GWR130-11	30	70	Asbestos	7800	5.3	3.50	14,120	8.34	19,620	3.12	.111
3GWR130-10			3GWR120	7065	4.8	2.68	13,210	6.68	22,240	2.90	.104
4GWR16-5			3GWR106-1	4860	1.3	5.31	23,470	17.5	23,800	6.99	.118

* Flexural and Compressive properties were determined with unconventional samples. The data is reliable only for internal comparison.

(1) psi

(2) psi x 10^5

(3) psi x 10^4

(4) Sample thickness is inversely proportional to density. Flexural and compressive properties should have higher values with increased density or decreased thickness.

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STATUS REPORT

INORGANIC POLYMERS:

IMPACT MODIFICATION OF ASBESTOS-

PHOSPHORIC ACID COMPOSITION BOARD

Authors: G. D. Jacobs
J. A. Faucher

Date: July 6, 1964

Project No.: 191G31

File No.: 2777

SUMMARY: The work on this project has been concerned mainly with the inorganic mineral chrysotile, a form of asbestos currently being mined by the Nuclear Division at Coalinga, California. Attempts have been made to impact modify an asbestos-phosphoric acid-water composition board (code designation P-38) originally produced by the Nuclear Division. Previous experience here had shown that impact strength correlated well with low temperature "transitions" in the mechanical loss spectrum of organic polymers, and it was felt that the incorporation of one of these organic polymers in the asbestos board might lead to the desired product. To date, however, the addition of a rather large number of organic polymers in various percentages has not improved the strength of the board to any great extent. It is now felt that some material will be necessary that is capable of chemically reacting with the hydroxyls of either the asbestos or the phosphoric acid. Very little is known about the chemical reaction between the asbestos and phosphoric acid. In fact, the physical characteristics of the asbestos fibers are still open to controversy and a great deal of basic research is currently being carried out on this material. A brief sampling of some of this work is given in this report.

Present work on this project to modify the P-38 composition is concerned with the possibility of adding fibrous organic polymers to the mixture. This phase of the work is a direct result of the work carried out by the U.S. Army on the addition of nylon fibers to cement in which they were able to improve the impact strength of cement by a factor of twenty-seven. Preliminary work with asbestos shows an increase in impact strength, although not nearly as large as in the case of cement. Projected work includes the use of polycarbonate and polyhydroxyether fibers as additives.

INTRODUCTION: Asbestos is the generic name given to a number of mineral silicates varying quite widely in chemical composition. These silicates are divided into two mineral classes; serpentine and amphibole. A list of the more common types is presented in Table I along with their chemical formulae.

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By far the most important single type of asbestos is chrysotile, accounting for nearly 90% of world production. Certain ones of the amphibole group, noteably crocidolite (blue asbestos), amosite, and anthophylite, do find use in specialized plastics applications[1,2].

The major portion of this report is concerned with a chrysotile variety being mined by the Nuclear Division at Coalinga, California. Table II is a comparison of the physical properties of a general chrysotile asbestos with the high-purity grade UCC Coalinga fiber.* The unique properties of the Coalinga fiber are attributed to its greater specific surface area and adsorption properties as shown in the table.

Chemically, chrysotile has been described as a hydrated basic silicate of magnesia. Normally, some magnesium carbonate and hydroxide are associated with the fibers in the form of dolomite and brucite. Table III gives the chemical and mineralogical compositions of a general chrysotile fiber as compared to the Coalinga fiber.

Until a few years ago the formula for chrysotile was written as $3MgO \cdot 2SiO_2 \cdot 2H_2O$, implying a di-hydrate. As a result of recent research efforts[3,4,2], it is now felt that a better representation of the "molecule" is given by the formula $Mg_3Si_2O_5(OH)_4$, where the previous water molecules are now present in the form of hydroxyl groups. The individual fibers are pictured as layers of silicon-oxygen tetrahedra ($Si_4O_{10}^{-4}$) condensed onto magnesium hydroxide layers. Each of the silicon-oxygen/magnesium hydroxide layers is superimposed upon layers of similar composition, but no chemical bonding is thought to occur between the layers. A schematic drawing of a portion of the curved wall layer of a chrysotile fiber is shown in Figure 1 [5]. Another view is shown as Figure 2.

A controversy has also arisen over the physical structure of the individual fibrils. Pictures taken with the electron microscope seem to indicate that the fibers are in the form of "hollow tubes"[6]. Recent evidence from X-ray diffraction measurements[5] and density determinations[7] has thrown doubt on this theory and the present proposed picture is that the central portion of the tubes is filled with amorphous or partially oriented material. As pointed out by Dr. E. J. W. Whittaker this filling of the tubes with amorphous material would lead to an appearance of emptiness under the electron microscope due to the contrasting effect between the walls of the fiber and the filling material. A recent study using ultrasonics[8] also provides evidence that the material filling the voids between fibers is amorphous.

Chemical reactions of chrysotile are also now being investigated. X-ray methods serve as the principal tool for studying these hydrothermal reactions, which are found to be predominantly topotactic. Being topotactic implies that the normal reaction involves the migration of cations, including silicon, while having little effect upon the oxygen framework[9,10].

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* Three product grades of asbestos are currently available from the Nuclear Division: Standard Grade, High Purity Grade, and Colloid

The preceding paragraphs should serve as a general introduction to the nature of the mineral asbestos and give some idea of the research being done on this material. Further specific information may be found in the references cited as well as in the four books listed in the bibliography.

Due primarily to the large supply available and to the unique characteristics of Coalinga fiber, the Nuclear Division initiated work on finding saleable products which utilized their asbestos. One of the materials produced was an asbestos-phosphoric acid-water composition board (code designation P-38),[11]. This material suffered, however, from a lack of impact strength as well as poor weatherability. The Nuclear Division also developed an asbestos-phenolic composition (code designation F-100) which showed both improved strength and weatherability[12]. Efforts at Tuxedo have since been directed primarily at improving and marketing the F-100 composition in the form of pipe.

Since previous experience was available on impact strength of organic polymers, as evidenced by studies on the low temperature loss peaks in the mechanical loss spectrum, it was decided to look again at the P-38 compositon with the thought of adding an impact modifying filler to the composition.

Experimental

The Coalinga asbestos used throughout these investigations was the high-purity grade - i.e. the material has been defilibrated and the magnetite removed. Early experiments were concerned with finding the best ratio of asbestos-phosphoric acid-water for easy mixing and extrusion. After several trials using various ratios,it was found that the following proportions were most satisfactory:

70 parts asbestos
35 parts water
30 parts 85% phosphoric acid

The dry, powdery asbestos is loaded into a Cincinnati Mix-Muller* and the phosphoric acid-water solution added through a funnel provided with the mix-muller. The time taken for addition of the phosphoric acid-water solution is rather critical in that water is apparently lost from the mixture for both short times of addition (causes heating of the mix) and also by evaporation if excessive time is involved. We have found, in agreement with the Nuclear Division, that a fifteen-twenty minute period for addition of ingredients is best. Additional ingredients were normally added after the phosphoric acid-water solution and in certain cases (liquid fillers) a proportionately smaller amount of water was necessary in order to acquire an extrudable product. The final product, ready for extrusion, is of a putty-like consistency.

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*Cincinnati Muller Co., Cincinnati, Ohio; Previous experiments had shown that a Hobart blender did not give adequate mixing on this scale (2 lbs asbestos)

The first experiments (before acquisition of an extruder) with the P-38 composition consisted of pressing the material into disc-shapes at 10,000 psi. Tests on these discs showed, however, that in order to obtain material with any strength whatever it would be necessary to extrude the composition. Previous work by the Nuclear Division (see reference 11) had shown that a ram-type extruder was best suited for the P-38 composition.

The ram extruder now in use was designed by Mr. Gene LeRoy of the Research and Development Department Special Projects Division, Machine Design. An Ener Pac* hydraulic, power-operated, pump and cylinder are incorporated in the design. The exit die is of a rectangular shape with dimensions 3" x $^1/_4$".

The P-38 composition is loaded into the extruder and then the ram moved forward to seal-off the chamber. The chamber is evacuated for several minutes before the extrusion is started. Starting with two pounds of asbestos, an extruded "board" approximately four feet in length is obtained (3" in width, $^1/_4$" in thickness). Normal extrusion pressure is 2000-3000 psi.

The "board" is cut into six and twelve inch lengths. The six inch lengths are rolled out (transverse to direction of extrusion) into pieces $^1/_8$" in thickness, using several passes through a large roll mill. All the pieces are then subjected to a room temperature cure followed by a cure at either 110°C or 150°C depending on the type of filler used. It is necessary during the cure-cycle to sandwich the asbestos strips between expanded-metal sheets in order to prevent warping.

After curing, the boards are removed from between the metal sheets and cut into small pieces for testing. The $^1/_8$" thick samples are given flexural strength and flexural modulus tests (ASTM D790-61) while the $^1/_4$" specimans are subjected to the Izod impact test (ASTM D256-56). The Gardner impact test proved unsatisfactory for testing these specimans. All samples are tested in both the parallel and transverse directions (designated P and T respectively in the tables).

DISCUSSION: The first experiments with the P-38 blend were concerned with finding the best ratio of ingredients and optimum mixing time, as pointed out in the experimental section of this report. A short study was also conducted to determine the function of room temperature curing time on the strength of the final board. Previous studies by the Nuclear Division had shown that both a room temperature cure and a final curing at an elevated temperature were necessary for a high-strength board. The results of our room temperature cure-time study are given in Table IV and shown plotted in Figure 3. From these results, it was concluded that a room temperature cure of at least sixteen hours was required. The three points shown plotted for a sixteen hour cure were taken as an indication of the deviation which can be expected from one batch to the next. Several runs were also made using different curing temperatures as well as different amounts of time at this elevated temperature but

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* Blackhawk Industrial Products Co., Butler, Wisconsin.

all seemed to indicate that 16+ hours at room temperature followed by 4 hours at 150°C gave the best results.

The next step in the project was to investigate the effect which various additives would have on the strength of the P-38 composition. The rest of the discussion section will be sub-divided into sections dealing with the various additives thus far investigated.

DQDA 3269 (72/28 ethylene/vinyl acetate copolymer)

An informal report by Dr. G. H. Potter (Project No. 399M20; dated 16 December, 1963) reported the possibility of cross-linking or reaction of some type between asbestos and ester-containing polymers, after mixing on a hot roll-mill. Unfortunately this method coats the asbestos fibers so that they are no longer available for attack by the phosphoric acid-water solution used in the P-38 composition. Even prolonged extraction with toluene did not remove enough of the excess polymer so that the fibers could undergo further chemical reaction. An attempt was also made by first reacting approximately one-half of the phosphoric acid-water solution with the asbestos and then placing the material on the mill with DQDA. However, the DQDA would not react in this case and was present in the extruded board as an inert filler. Adding pulverized DQDA to the mixture in the mix-muller was also unsuccessful.

One further step was taken with this type polymer. Granulated AYAT was added to the dry asbestos in the mix-muller followed by the phosphoric acid-water solution. The AYAT appeared to be present as an inert filler also.

Hercules "Aquapel" (364 and 380)

The next material tried was "Aquapel", an alkylketene dimer manufactured by Hercules Powder Company. The dimer was added both in the form of dry flakes and as an emulsion in water. As can be seen from Table V, no significant increase in the strength of the P-38 composition was obtained.

Cationic Wet-Strength Resin

A cationic wet-strength resin consisting of poly β-asparagine polyamine partially crosslinked with epichlorohydrin (14.2% total solids) was obtained from Dr. P. M. Westfall and added to the standard P-38 mixture. The material before curing is very difficult to break apart but as shown in Table V, after curing it shows no great improvement in strength or impact.

Gantrez AN-139 Copolymer

As a result of reading U. S. Patent 3,113,064 entitled, "Asbestos paper containing vinyl alkyl ether-maleic anhydride copolymer and method of forming same", we decided to try adding one of these copolymers to the P-38 mixture. The one chosen was Gantrez AN-139, a copolymer of methyl vinyl ether and maleic anhydride manufactured by General Aniline and Film Corporation (gaf). The copolymer was

added both in the dry state and in the form of a water dispersion. There was some improvement in the strength of the cured P-38 board but not a significant amount. (see Table V).

Polyox - Carbopol 940

Carbopol 940 is a water-soluble, high molecular weight poly (acrylic acid) manufactured by the B. F. Goodrich Chemical Company. The Polyox and Carbopol were added to the asbestos in the mix-muller both in the dry state and as a mixture in water. A combination of Polyox and Carbopol was also tried but did not give any great improvement in strength as seen in Table V.

Latexes

Since the best way to obtain good dispersion of the filler material and at the same time enhance the possibility for any reaction between the filler and the asbestos is to add the filler as a water solution, the use of latexes becomes a logical possibility.

After a few batches were prepared, it became apparent that a new study of strength as a function of curing time and temperature was needed. A series of mixtures were prepared using as a filler 10.4% of a 60/40 styrene/butadiene latex containing 48% total solids. The variables included room temperature cure times of from 0 to 36 hours and high temperature cures (110°C) of 4,8,16, and 32 hours. The results are tabulated in Table VI and shown plotted in Figure 4. As a result of this study, the remainder of the runs using latex fillers involved room temperature cure times of 30+ hours followed by 24 hours at 110°C.

As can be seen from Table VII, various types and percentages of latexes were studied, including styrene/butadiene, polyethylene/acrylic acid, phenoxy A, and a carboxylic modified butadiene/acrylonitrile copolymer (a product of the Chemical Division of The Goodyear Tire and Rubber Company, known commercially as Chemigum Latex 550). Again, however, no really outstanding improvement in strength was obtained for any of the latexes used as fillers.

Di-(2-ethylhexyl) phosphoric acid

In place of a portion of the phosphoric acid used in the P-38 composition, di-(2-ethylhexyl) phosphoric acid was substituted. It was hoped that some cross-linking could be promoted by using this material but in all the mixes prepared, the cured board was extremely weak. The use of superphosphoric acid was also investigated but it proved unsuccessful. No testing of these samples was attempted.

Fibrous fillers

The use of fibrous fillers has proved to be the best choice to date. As shown in Table VIII, crocidolite (Cape blue asbestos), glass, and nylon fibers have been tested and they all seem to increase impact strength, especially the nylon. The work on nylon stems from

a report by the U. S. Army[13] on the addition of nylon fibers to cement. The impact strength of cement is reported to be increased by a factor of twenty-seven.

Further work is being planned along these same lines using as fillers, nylon (different denier), polycarbonate, and polyhydroxy-ether fibers.

F-100 Composition

For comparison purposes, a batch of the F-100 composition was prepared and tested. The ingredients were as follows: 60 parts asbestos, 15 parts water, and 25 parts BRL 1100 (water soluble phenolic predominating in dimerized trimethylol phenol with some residual monomer; 64-68% solids content). The test results are listed in Table VIII.

Gerald D. Jordan

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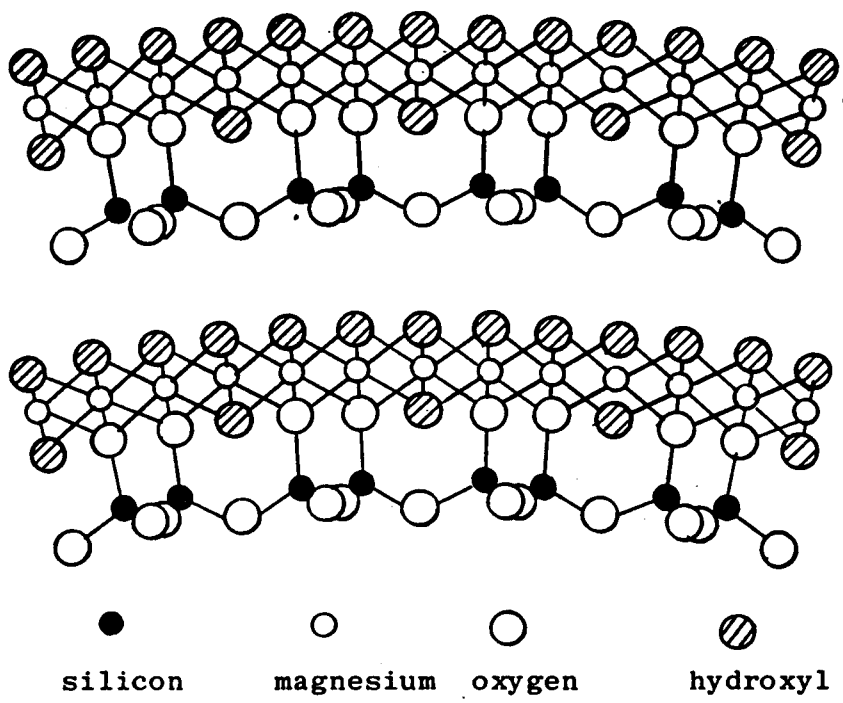
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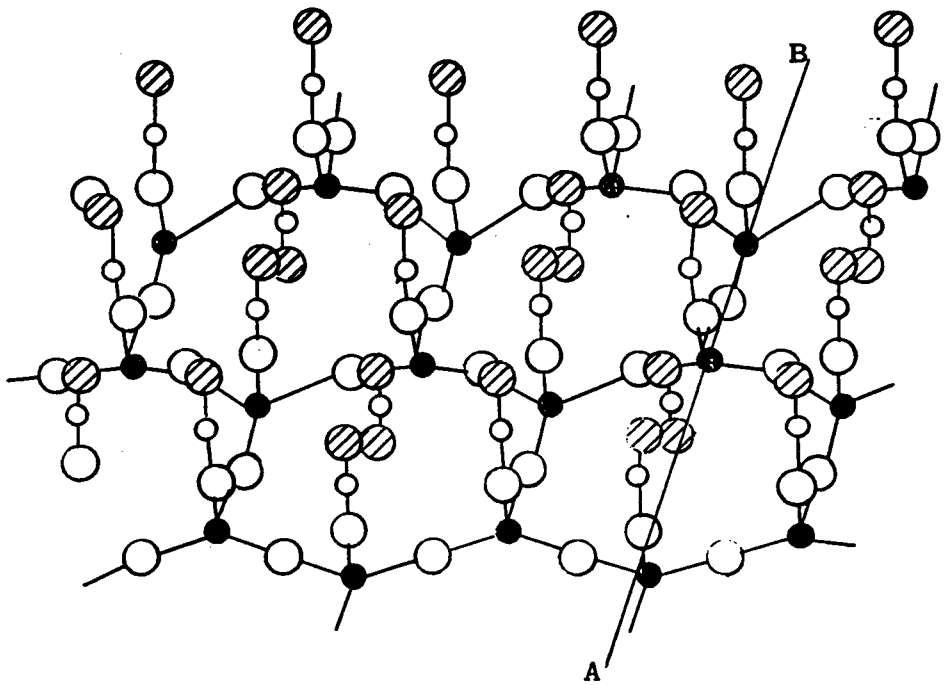
Figure 1*



* Chem. and Eng. News. p. 35, 30 Sept. 1963

This drawing represents a portion of the curved wall layer of a fiber of chrysotile asbestos. The fiber walls are composed of 12 to 20 such layers; each layer being about 7.3 Å thick.

Figure 2



- silicon
- magnesium
- oxygen
- hydroxyl

The line $\overline{AB}$ parallels one of the layers shown in Figure 1.

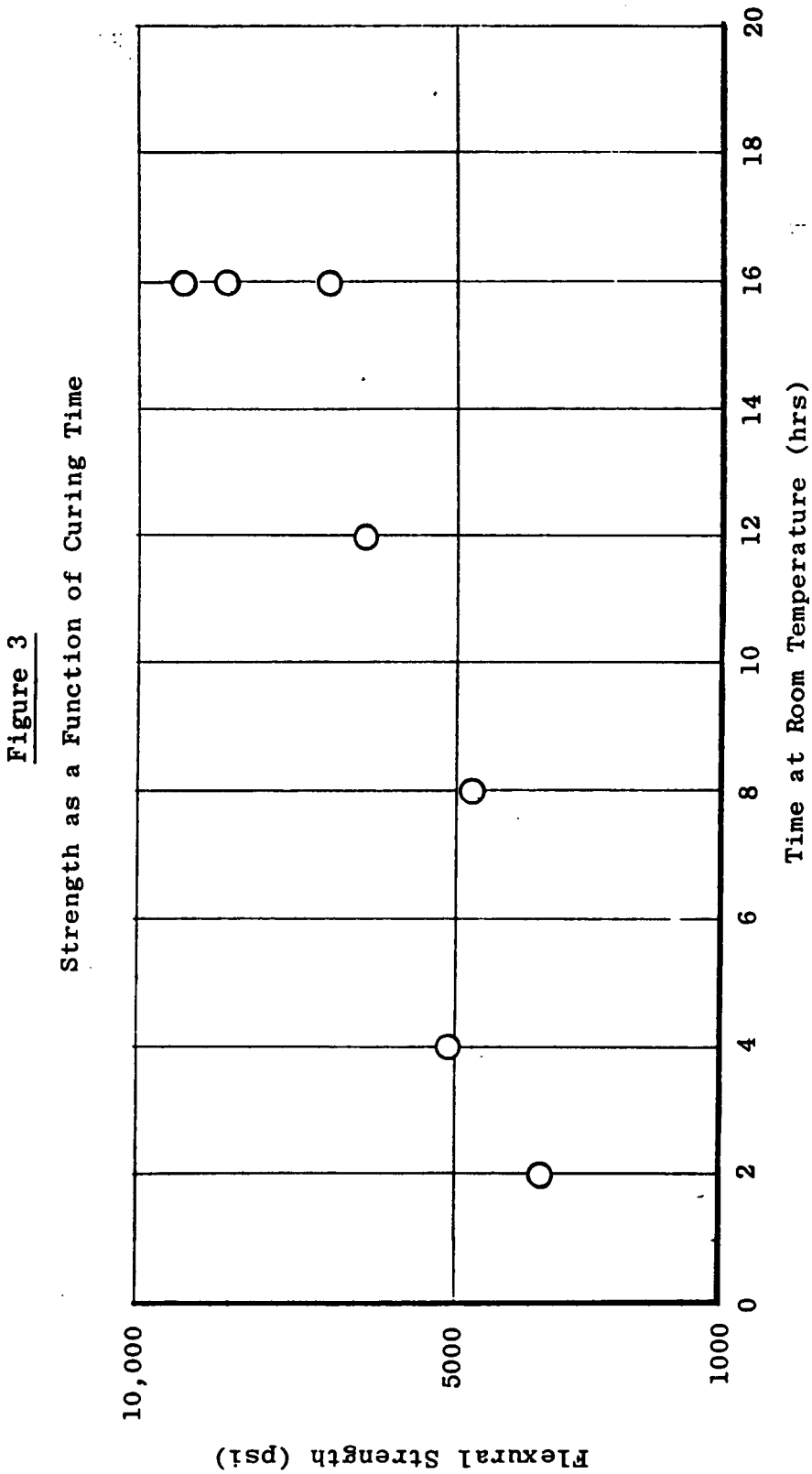


Figure 3

Strength as a Function of Curing Time

Figure 4

Flexural Strength vs Time at Room Temperature

(all samples received later cure of 16 hrs at 110°C)

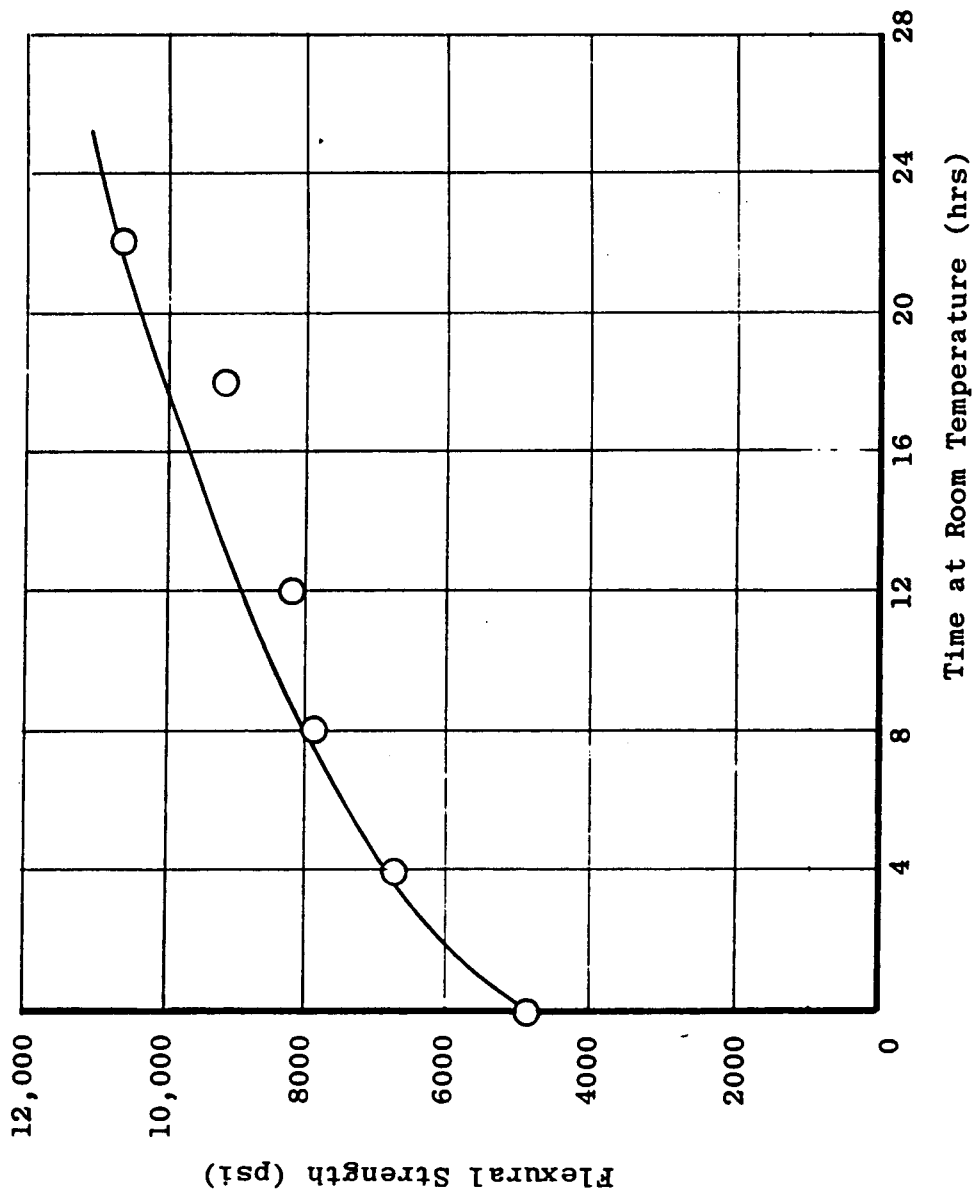


TABLE I

Classification	Common Name	Formula
Serpentine	Chrysotile*	$Mg_3Si_2O_5(OH)_4$
Amphibole**	Crocidolite	$Na_2Fe_5Si_8O_{22}(OH)_2$
	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
	Actinolite	$Ca(MgFe)_5Si_8O_{22}(OH)_2$
	Anthophyllite	$(MgFe)_7Si_8O_{22}(OH)_2$
	Amosite	$(MgFe)_6Si_8O_{22}(OH)_2$

---

* chrysotile exists in at least three modifications depending upon the form of the crystal lattice. The following four papers are recommended for the interested reader.

1. E. J. W. Whittaker, Acta Cryst. 6, 747 (1953)
2. E. J. W. Whittaker, Acta Cryst. 9, 855 (1956)
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4. E. J. W. Whittaker, Acta Cryst. 9, 865 (1956)

** for more information on the crystal chemistry of amphiboles see:

5. E. J. W. Whittaker, Acta Cryst. 13, 291 (1960)

TABLE II*

Property	General Chrysotile Asbestos	UCC Coalinga Asbestos (high-purity grade)
Density, g/cc	2.25-2.75	
Hardness	2.5-4.0	
Specific Surface m^2/g	10-50	60-70
Oil Adsorption g/10g	4-5	14-16
Water Retention g/20g	32-34	
Bulk Density		
Wet cc/5g		175+
Dry lb/ft^3	10-15	3-5
Refractive Index	1.50-1.55	
Luster	silky	
Color	green-gray	white
Brightness (% of MgO)		75-80
Electrical Charge	positive	
Acid Resistance	poor	
Alkali Resistance	good	
Specific Heat BTU/lb-°F	0.266	
Tensile Strength lb/in^2	80,000-100,000	
Temp. of Max. Loss	800°C	
Temp. of Struct. Loss	600°C	

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* Table taken from letter of W. H. Dresher, Nuclear Division

TABLE III*

CHEMICAL COMPOSITION

Compound		General Chrysotile Asbestos	UCC Coalinga Asbestos (high-purity grade)
MgO		36-44%	42
SiO_2		35-44	42
Fe_3O_4		0.5-5.0	<1.0
Fe_2O_3		0-6.0	--
FeO		0-6.0	0.3-1.6
H_2O	Total	12-15	16.0
	Combined	--	13.5

MINERALOGICAL COMPOSITION

Mineral	General Chrysotile Asbestos	UCC Coalinga Asbestos (high-purity grade)
chrysotile	major	major
brucite	moderate	minor
magnetite	0.5-5.0%	<1.0%
hydrotalcite	--	minor

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* Table taken from letter of W. H. Dresher, Nuclear Division

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TABLE IV

Study of Strength as a Function of Curing Time

Notebook Reference 5808-	Curing Time (hours)		Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
			P*	T*	P	T	P	T	
	25°C	150°C							
27-1	2	4	3692	3729	1.61	1.34	0.15	0.12	1.36
27-2	4	4	5171	3981	2.57	1.76	0.16	0.31	1.44
28-1	8	4	4808	3919	2.44	2.05	0.14	0.13	1.48
28-2	12	4	6488	4630	2.89	2.39	0.14	0.17	1.63
25-1	16	4	7059	5562	3.46	2.11	0.13	0.14	1.57
25-2	16	4	8662	6250	3.20	2.64	0.16	0.14	1.57
45-2	16	4	9306	8484	2.86	2.49	0.28	0.20	1.53

Ingredients: 70 parts asbestos; 35 parts water; 30 parts phosphoric acid (85%)

*P - parallel direction, T - transverse direction

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TABLE V

P-38 Composition Plus Additives

Notebook Reference 5808-	Additive*	Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
		P	T	P	T	P	T	
38-1	4.7% Aquapel (emulsion)	4431	4280	1.27	1.18	0.17	0.11	1.44
37-1	4.7% Aquapel (dry flakes)	5076	3759	2.36	1.57	0.17	0.14	1.43
41-2	14.4% Cationic wet-strength resin	7680	7563	1.80	1.75	0.16	0.14	1.55
41-1	28.7% Cationic wet-strength resin	7317	7078	1.76	1.73	0.15	0.14	1.55
62-1	0.3% Gantrez AN-139 (dispersion)	8501	5922	2.66	2.08	0.24	0.18	1.60
62-2	1.3% Gantrez AN-139 (dispersion)	8118	9795	2.61	2.58	0.22	0.17	1.57
63-1	1.3% Gantrez AN-139 (dry)	8295	7716	2.66	2.38	0.27	0.22	1.52
34-1	1% Polyox (coagulant grade)	8083	6553	1.89	1.63	0.17	0.19	1.55
69-1	0.3% Carbopol 940	8329	6733	3.09	2.66	0.28	0.19	1.62
69-2	0.6% Carbopol 940	9589	6964	2.94	2.70	0.24	0.19	1.58
70-1	1.3% Carbopol 940	8076	6019	3.01	2.45	0.25	0.18	1.63
72-1	0.3% Carbopol + 0.3% Polyox	5927	3908	2.29	1.83	0.43	0.14	1.51
72-2	0.6% Carbopol + 0.6% Polyox	4525	4652	2.07	1.83	0.29	0.16	1.52

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* percentages are based on initial charge of ingredients (i.e. before curing)

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TABLE VI

P-38 Composition Plus Additives

Notebook Reference 5808-	Additive* 10.4% of a 60/40 styrene/butadiene latex; 48% total solids		Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
	Curing Times		P	T	P	T	P	T	
	room.temp.	110°C							
48-4	0 hrs.	8 hrs.	4787	4447	2.45	1.83	0.20	0.17	1.44
48-3	0	16	4861	4520	2.21	1.97	0.21	0.15	1.45
47-2	2	8	5671	5123	2.09	2.01	0.22	0.30	1.47
48-2	4	8	6682	6025	2.27	2.14	0.24	0.23	1.49
48-1	4	16	6726	5872	2.57	2.13	0.21	0.24	1.54
49-4	8	8	7303	6948	2.23	2.04	0.23	0.20	1.51
49-3	8	16	7934	6662	2.29	2.06	0.23	0.34	1.51
47-1	12	4	7197	6417	2.12	2.14	0.27	0.21	1.55
49-2	12	8	9014	7906	2.52	2.26	0.25	0.18	1.55
49-1	12	16	8211	8183	2.96	2.43	0.28	0.32	1.60
49-8	16	8	8753	7790	2.70	2.27	0.23	0.18	1.58
49-7	18	16	9233	8251	2.47	2.34	0.24	0.18	1.57
49-6	20	8	9722	9416	2.56	2.49	0.25	0.20	1.57
49-5	22	16	10,695	8843	3.00	2.61	0.24	0.20	1.57

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* percentages are based on initial charge of ingredients (i.e. before curing)

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TABLE VII

P-38 Composition Plus Additives

Notebook Reference 5808-	Additives* (latexes)	Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
		P	T	P	T	P	T	
42-1	2.6% 60/40 S/B (48% total solids)	8600	7360	2.73	2.28	0.22	0.17	1.61
42-2	10.4% 60/40 S/B (48% total solids)	8361	7535	2.35	2.14	0.23	0.17	1.58
45-1	20.7% 60/40 S/B (48% total solids)	5833	5062	1.72	1.48	0.26	0.36	1.47
53-1	9.9% 60/40 S/B; 4.7% ZnO	5629	4908	2.22	2.27	0.18	0.16	1.54
53-2	10.2% 60/40 S/B; 2.5% Sulfur	6954	6835	2.36	2.40	0.20	0.17	1.59
44-1	2.6% 50/50 S/B (51.5% total solids)	8156	7850	2.73	2.40	0.20	0.17	1.55
44-2	10.4% 50/50 S/B (51.5% total solids)	7427	6827	2.34	2.20	0.22	0.19	1.56
44-3	20.7% 50/50 S/B (51.5% total solids)	4682	4824	1.46	1.38	0.43	0.21	1.43
67-2	2.6% 45/55 S/B (50% total solids)	9444	8434	2.76	2.54	0.22	0.20	1.63
52-1	10.4% 45/55 S/B	7746	6812	2.34	1.89	0.21	0.17	1.54
46-1	2.6 % polyethylene-acrylic acid latex (7% acrylic; 47.4% total solids)	9415	7842	3.21	3.10	0.25	0.26	1.56
46-2	10.4% " " "	8874	8524	2.50	2.34	0.27	0.28	1.54
55-1	2.6% PE-AA, (15% acrylic; 40% total solids)	8535	7409	2.79	2.54	0.25	0.16	1.59
58-1	10.4% PE-AA, (6% acrylic; 48% total solids)	6977	6507	2.40	2.15	0.17	0.13	1.42
71-1	2.6% phenoxy latex (38% total solids)	4721	3908	1.91	1.78	0.20	0.15	1.49
71-2	5.2% phenoxy latex (38% total solids)	4607	3677	1.83	1.71	0.22	0.17	1.49
71-3	10.4% phenoxy latex (38% total solids)	4580	4101	1.50	1.58	0.18	0.14	1.43
73-2	2.6% Chemigum 550 (38.1% total solids)	5035	3579	2.34	1.77	0.17	0.17	1.54
76-1	5.2% Chemigum 550 (38.1% total solids)	5606	4824	2.41	1.99	0.21	0.17	1.51
76-3	10.4% Chemigum 550 (38.1% total solids)	6608	5760	2.18	1.94	0.24	0.21	0.92
76-4	9.85% Chemigum + 4.92% ZnO	5031	4807	1.45	1.42	0.17	0.15	1.47

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* percentages are based on initial charge of ingredients (i.e. before curing)

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TABLE VIII

P-38 Compositon Plus Additives

Notebook Reference 5808-	Additive	Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
		P	T	P	T	P	T	
26-1	2.8% crocidolite (blue asbestos)	5716	5064	2.64	2.19	0.36	0.25	1.47
26-2	2.8% 1/4" glass fibers	5892	3464	2.77	1.88	0.24	0.14	1.48
30-1	2.8% 1" glass fibers	4587	2691	1.09	0.73	0.32	0.13	1.30
68-1	0.5% 1"-3" nylon fibers (140 denier)	6834	6709	2.66	2.64	0.42	0.17	1.61
68-2	0.3% 1"-3" nylon fibers (140 denier)	8834	6966	2.93	2.24	0.42	0.52	1.62
79-1	F-100 composition	13,912	12,562	2.33	1.91	0.27	0.22	1.59

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