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NEW ENTERPRISES

ASBESTOS REINFORCED RESINS

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SUMMARY Chrysotile asbestos and aqueous acids react in two ways: the acid is neutralized by a magnesium hydroxyl group and is retained in the asbestos; the acid is neutralized, and the magnesium salt is dissolved or precipitated in the water layer. Very weak acids, such as magnesium dihydrogen diphosphate, give the first effect. Intermediate acids, such as acetic acid, give both effects and incomplete reaction. Strong acids, such as hydrochloric acid, give the second effect which is stoichiometrically complete.

Dibasic and tribasic acids, which have a wide spread in ionization constants, have been used as cross-linking agents for asbestos. These materials, however, disrupt the asbestos structure by extracting magnesium prior to cross-linking through the weaker acid groups. The effect on resin properties of partially neutralizing these acids before mixing with asbestos will be investigated. Since water is required in these reactions, more satisfactory techniques for molding and curing must be sought.

STRUCTURE OF ASBESTOS In the last report the re-occurring formula unit of asbestos was given as $Mg_6(OH)_8Si_4O_9$. The magnesium-hydroxyl attack points on the molecule were considered to be six (≥Si-OMgOH) groups per re-occurring asbestos unit. In view of more enlightened information since obtained from Sterling Forest and elsewhere on the structure of asbestos, this assumption is not strictly true. Originally it was supposed that the siloxane bulwark of the molecule was a chain of connected duodecagons of the structure shown in Figure I. This configuration leaves six unsatisfied silicon bonds to carry the six (OMgOH) groups. Actually, however, the siloxane nucleus is not a chain polymer as shown but a "sheet" polymer of interlocking duodecagons, as indicated in Figure II. It can be seen with this configuration only one valence of each silicon is unsatisfied, or four bonds per re-occurring formula unit are available to hold 6-Mg's, 5 extra O's, and 2 extra OH's. (8-6). It is obvious then that conventional full valence bonding cannot be applied here and apparently the coordinate bonding of magnesium is involved. It also appears that magnesium atoms, holding

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of acid per formula weight of asbestos $Mg_6(OH)_8Si_4O_9$ is present, this reaction will continue until all the magnesium has been removed and only a siloxane residue remains. If less than 12 equivalents of acid per formula weight are present, however, the reaction will continue until (1) all the acid is neutralized, (2) the atoms of magnesium solubilized will be one-half the equivalents of acid reacted and (3) the remaining magnesium atoms and their accompanying hydroxyl groups will be left in the asbestos molecule untouched. In short, the reaction of "strong" acids with asbestos can be considered as their essentially instantaneous action of $2H^+$ ions to remove a magnesium atom from the molecule. This group includes, in addition to the totally ionized acids, other polybasic acids whose "first hydrogens" are relatively strong such as maleic (1.4×10^{-2}) and phosphoric acid (7.5×10^{-3}). Data obtained using maleic acid are shown in Table IV and V and for phosphoric acid in Table III.

2. Acids in the 10^{-5} Range of Dissociation Constant

The conventional straight chain organic acids (acetic, butyric, adipic, succinic, etc.) are included in this group. Their chemical action on asbestos departs markedly from that of the strong acids and (based chiefly on the behavior of acetic acid) may be characterized as follows:

(1) Their reaction with asbestos is never complete even when very high excess concentrations of acid and temperatures of 100-108°C are employed. Reaction of 40-50% of the magnesium is easily and quickly obtained at concentrations of 6-24 mols of acid per formula weight of asbestos. As concentration of acid is increased the maximum reaction point rises slowly until at 60 mols acid concentration 70-75% reaction of magnesium is obtained. Data for these various concentrations of acetic are given in Table VI.

(2) While substantial magnesium cleavage does occur in reactions with these acids, it approaches stoichiometric quantities only when large excesses of acid are employed and is relatively low when less than theoretical concentrations are employed. For example with acetic acid, when 6.0 mols of acid per formula weight of asbestos is used, only 14% of the magnesium reacted is cleaved from the asbestos molecule.

These data for acetic acid are summarized in Table VII. These data, together with other fragmentary data obtained at lower temperatures, suggest that, with the proper selection of acid concentration, time and temperature, considerable pendant group attachment might be accomplished with a minimum of magnesium cleavage. More data will be obtained on this important point.

From these data for the action of acetic acid, a wide difference in reactivity of magnesium atoms (or probably more correctly their attached hydroxyls) is indicated, since roughly 40-50% of the magnesium is attacked rather readily, but approximately 25% can probably not be attacked at all. It is also evident that

the cleaving reaction by the "second" mol of acid lags considerably behind the reaction of the "first" mol which simply couples by neutralization.

3. Acids in the 10^{-7} to 10^{-8} Range of Dissociation Constant

When the dissociation constants of acid groups are in the low range of 10^{-7} to 10^{-8}, reaction will occur with the more reactive asbestos hydroxyl without any discernible magnesium cleavage. This conclusion is based on data collected for the action of the "second" H^+ ions of maleic ($8{,}6 \times 10^{-7}$) and phosphoric (6.2×10^{-8}) acids in the cross-linking of asbestos. A more detailed discussion will appear later in the report. (See Tables III, IV, and V.)

NONAQUEOUS ACID REACTIONS Limited investigation of the reaction of maleic acid with asbestos in refluxing ketones (80-140°C.) as solvents indicates very low reaction rates and maximum reactions of only 15-20%. In addition, magnesium is cleaved in stoichiometric quantities. This approach, therefore, is not promising. Data obtained in methyl ethyl ketone is shown in Table VIII and in cyclohexanone in Table IX.

CROSS-LINKING OF ASBESTOS WITH DIBASIC ACIDS From the foregoing discussion of the action of "strong" acids on asbestos it is evident that in the cross-linking of asbestos with either maleic or phosphoric acids, the "first" H^+ ions can only cleave magnesium from the molecule. It follows then that the cross-linking must be accomplished by the "second" H^+ ions of the acid salts formed by the cleavage reaction. With maleic acid, the acid salt would be magnesium dihydrogen dimaleate, $Mg(OOCCH{=}CHCOOH)_2$ and for phosphoric acid, magnesium tetrahydrogen diphosphate $Mg(H_2PO_4)_2$. Chemical analyses made during actual cross-linking experiments with the two acids confirmed this conclusion. This consideration lead to the attempted preparation and isolation of the two salts for their subsequent use as cross-linking agents. Although the $Mg(H_2PO_4)_2$ was not isolated, a hydrated form of the maleic salt was obtained and employed in several cross-linking experiments. This cross-linking method has the advantage over the use of the acid and asbestos directly, of bringing the more reactive hydroxyls into play in the cross-linking reaction. Otherwise these reactive hydroxyls are wasted in making the magnesium salt by cleavage before cross-linking occurs.

In one instance a highly cross-linked product (97.7% of carboxyl reacted) was prepared in the form of a patty by this method. The ratio of carboyl/unit formula of asbestos was 1.33 or 4.5 hydrols to each carboxyl. This product was extremely hard and had fair water resistance. Other attempts using the same ratios but different curing conditions were not as successful, although one sample, prepared in the form of a cylinder (68% of carboxyls reacted) showed 1900 lbs/sq.in. compressive strength. The rate of temperature rise (with the resulting removal of water) versus the rate of cure is optimum within narrow limits for this reaction, due to the limited solubility of the salt in water (approximately 5%

at 25°C and probably 25% at 80°C.). The large amount of water which must eventually be removed from the cured specimens (50-65%) makes it difficult to maintain formed shapes during curing. This disadvantage, because of the lower water content, is not so pronounced in the phosphoric acid reaction and further work is planned with this acid employing an acid salt prepared and left in solution.

In summarizing acid cross-linking, it might be pointed out that the products prepared from either maleic or phosphoric acids are rock-like in character and have considerable breaking strength. This was particularly true of the sample prepared from maleic salt which was almost completely cross-linked. This sample required repeated heavy hammer blows to break it. Lack of water resistance is a major problem with these products. Samples vary from fast disintegration in cold water in one hour, to slow surface disintegration after overnight soaking. At present the lack of equipment here to form definite shapes (as cylinders for compression testing), which do not contain numerous voids, is a definite handicap in completely evaluating the cross-linked products.

CONCLUSIONS The rate of reaction of an aqueous acid with asbestos varies directly with temperature, concentration, time, and acid ionization constant. Only strong acids (ionization constants of 10^{-3} or higher) react appreciably at 25°C. and stoichiometrically in boiling aqueous solutions. Strong acids serve only to cleave magnesium from asbestos. Only weak acids (ionization constants of 10^{-5} or lower, and preferably about 10^{-7}) are useful for attacking pendant groups and cross-linking. Even weaker aicds (e.g., phenols) may be capable of reaction. The minimum strength required for reaction is not yet known.

Although acids will react in the absence of water, reaction is appreciably facilitated by the presence of water.

The mechanism of cross-linking with dibasic acids having one strong and one weak acid group (e.g., maleic and phosphoric acids) involves 1) cleavage of magnesium to form a dibasic magnesium salt (e.g., $Mg(OOCCH{=}CHCOOH)_2$) and 2) neutralization of the acid groups of this salt by reaction with the remaining - MgOH groups of the asbestos. In order to prevent magnesium cleavage, it is advantageous to prepare the dibasic magnesium salt from magnesium hydroxide.

As a result of this study, several possible routes are suggested to the preparation of asbestos-containing compositions for use as pipe, formica-type laminates, building panels, printed circuits, and auto body patch kits. These reactions, which would cross-link the asbestos, are outlined via the following list of reactants:

1. Polybasic acids (e.g., $Mg(H_2PO_4)_2$, magnesium dimaleate, dimer acid, etc.).

2. Styrene + unsaturated acids (e.g., magnesium dimaleate acrylic acid and a carboxyl-capped polyester).

3. Polyphenols.

4. Diepoxides + polybasic acids.

5. Diepoxides (e.g., EP-206 with ammonium fluoborate catalyst).

6. Styrene + neutral esters of unsaturated acids (e.g., acrylic, methacrylic, and maleic).

7. Diisocyanates.

Other potential areas of application for asbestos are:

8. As coatings, modifiers for latexes, and molding powders after reaction with either a drying oil acid or acrylic acid.

9. Acid scavengers (e.g., as an HCl acceptor)for chemical reactions.

10. Soil conditioner for slow release of Mg into soil.

11. Fertilizer after reaction with $NH_4H_2PO_4$.

12. Flame-proof foams (taking advantage of the hydroxyl functionality of asbestos rather than using as an inert) by reaction with isocyanates.

EXPERIMENTAL In the study of the activity of acids in aqueous digestions, 30.0 gms. of asbestos in 700 cc of acid solution was employed. In the ketone digestions a ratio of 40 gms./ 500 cc was employed. With cross-linking experiments using phosphoric acid a recipe of asbestos 100 parts, 87% phosphoric acid 80 parts and water 25 parts, was employed. In maleic acid cross-linkings various ratios of materials were used but all within the following limits: Water 6-8 gms., maleic acid 12 gms and asbestos 16.3 to 30 gms. In the maleic salt cross-linking reactions a single recipe of water 90 gms., maleic salt 20 gms. and asbestos 51.0 gms. was used. The mixes in the cross-linking experiments were worked by hand and formed into "patties" for curing, except in one case where cylinders were formed by packing in glass tubes.

ANALYTICAL Magnesium content was determined by the method outlined in the report of April 8, which involves determining the amount of standard alkali necessary to precipitate the magnesium as hydroxide. "First" H^+ ion was determined by titrating with methyl red (pH range 4.4-6.2) as indicator; and "second" H^+ ion by finishing the titration with Phenolphthalein (pH range 8.3-10) as indicator.

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ATTACHMENTS: 9 Tables

L. C. Shriver/PLS

TABLE I

REACTION OF ASBESTOS WITH

AQUEOUS HYDROCHLORIC ACID AT 102°C.

(500 cc acid solution/30.0 gms asbestos. Equivalent data for acid given below are per formula weight of asbestos-554.)

Reference Number	Reaction time, hrs	Mols HCl Initially	Mols HCl At Reaction Completion	Mols HCl Reacted	Atoms Mg Solubilized	Mg x2
102LCS23-2	1.5	2.00	0	2.00	0.96	1.92
23-1	1.0	4.06	0	4.06	2.00	4.00
23-3	1.5	8.21	0	8.21	4.06	8.12
27	2.0	7.53	0.08	7.45	3.97	7.94
31	2.0	12.00	0.326	11.67	5.80	11.60

TABLE II

REACTION OF ASBESTOS WITH AQUEOUS HYDROCHLORIC ACID AT AMBIENT TEMPERATURES

(550 cc acid solution/40 gms. asbestos. Equivalent data for amounts of acid given below are per formula weight of asbestos-554)

REF. No. 102LCS43

Reaction Time, hrs	Mols HCl Unreacted	Mols HCl Reacted	Atoms Mg Solubilized	Mg x2
0	13.35	0	0	0
17.75	4.40	8.95	3.52	7.04
45.5	2.79	10.56	4.93	9.86
89.5	1.72	11.62	5.69	11.38
100.5	1.64	11.71	5.75	11.50

TABLE III

REACTION OF ASBESTOS WITH AQUEOUS PHOSPHORIC ACID AT BOILING TEMPERATURE (103°C.)

(500 cc aqueous phosphoric acid solution/30 gms. asbestos. Acid equivalent data given below are per formula weight of asbestos-554. Initial concentration of acid-6.065 mols acid/formula weight asbestos).

Ref. No.	Reaction Time Hrs.	Equivalents 1st H^+		Equivalents 2nd H^+	
		Unreacted	Reacted	Unreacted	Reacted
	0	6.065	0	6.065	0
	2.75	1.76	4.30	5.42	.64
	5.25	0	6.065	4.02	2.04
	10.75	0	6.065	2.83	3.23
	13.75	0	6.065	2.71	3.35

TABLE IV

REACTION OF ASBESTOS WITH AQUEOUS MALEIC ACID AT BOILING TEMPERATURE (103-106°C)

(500 cc maleic acid solution/30 gms asbestos. Acid equivalent data given below are per formula weight of asbestos-554.)

Reaction Time Hrs.	Equivalents 1st H^+ Unreacted	Equivalents 1st H^+ Reacted	Equivalents 2nd H^+ Unreacted	Equivalents 2nd H^+ Reacted	Atoms Mg Solubilized	Mg x 2
	102LCS14-A. Initial Concentration-601 mols maleic acid					
0	6.01	0	6.01	0	0	0
3	2.27	3.74	5.82	0.19	1.94	3.88
8	0.00	6.01	5.60	0.41	2.97	5.94
11	0.00	6.01	5.31	0.70	2.91	5.82
14	0.00	6.01	5.04	0.97	3.05	6.10
	102 14-B-Initial Concentration 4.25 Mols.					
0	4.25	0	4.25	0	0	
3	1.62	2.63	4.01	0.24	1.24	2.48
8	0.19	4.15	3.93	0.32	1.79	3.58
11	0.00	4.25	3.56	0.69	2.01	4.02
14	0.00	4.25	3.45	0.80	1.89	3.78

TABLE V

REACTION OF ASBESTOS WITH AQUEOUS MALEIC ACID AT AMBIENT TEMPERATURE.

(700 cc maleic acid solution/30 gms. asbestos. Acid equivalent data given below are per formula weight of asbestos-554.

REF. NO. 102LCS25
Initial Concentration 6.08 mols maleic acid.

Reaction Time, hrs.	Equivalents 1st H^+		Equivalents 2nd H^+		Atoms Mg Solubilized	Mg x 2
	Unreacted	Reacted	Unreacted	Reacted		
0	6.08	0	6.08	0	0	0
3.25	5.32	0.76	6.03	0.05	0.52	1.04
22.5	4.25	1.83	6.07	0.01	0.89	1.78
53.5	2.93	3.15	6.05	0.03	1.61	3.22
75.0	2.19	3.89	5.70	0.35	2.09	4.18
99.5	1.36	4.72	6.08	-0.03	2.29	4.58

REF. NO. 102LCS45
Initial Concentration 11.73 Mols Maleic Acid.

0	11.73	0	11.73	0	0	
17.25	8.71	3.02	11.59	0.14	1.36	2.72
43.75	6.76	4.97	11.73	-0.20	2.14	4.28
60.5	4.01	7.72	11.64	0.09	3.41	6.82

TABLE VI

REACTION OF ASBESTOS WITH BOILING

ACETIC ACID SOLUTIONS

(700 cc acetic acid solution/30 gms. asbestos)

Ref. No.	Reaction Time, Hours	Reaction Temp. °C.	Initial Conc. of Acid Mols/ Formula Weight Asbestos	Mols Acid Used/Formula Wt. Asbestos	Atoms Mg Solubilized Formula Wt. Asbestos	Mg x2
102LCS51	2.0	100	1.09	0.40	--	--
"	4.25	"		0.45	--	--
"	7.0	"		0.52	0.13	0.26
"	10.8	"		0.69	0.14	0.28
102LCS52	1.67	101	2.95	0.90	0.19	0.38
	4.25			1.19	0.33	0.66
	7.08			1.45	0.33	0.66
	11.00			1.64	0.35	0.70
	16.00			1.70	0.36	0.72
102LCS29	16.0	Ambient	6.03	0.39	0	0
"	5.75	102		3.23	0.37	0.74
"	10.0	102		3.48	0.745	1.49
102LCS37	3.0	103	12.0	4.30	1.80	3.60
"	8.0	103		4.48	1.95	2.90
102LCS38	3.0	105	24.0	5.14	2.55	5.10
	8.0	"		6.23	3.14	6.28
	16.0	"		6.35	3.20	6.40
102LCS39	6.0	108	60.0	7.35	3.68	7.36
"	22.0	"		8.10	3.85	7.70

TABLE VII

REACTION OF AQUEOUS ACETIC ACID

WITH ASBESTOS AT BOILING TEMPERATURE (100-108°C)

(700 cc of acetic acid solution/30 gms. asbestos)

Ref. No.	Approx. Time For Reaction Maximum Hrs.	Reaction Temp. °C	Initial Conc. Of Acid Mols/formula Wt. Asbestos	% Magnesium Attacked	% Mg Cleaved	Mg Cleaved / Mg Attacked %
102LCS51	10.8	100	1.09	9.6	2.3	24.0
52	16.00	101	2.95	22.2	6.0	27.0
29	5.75	102	6.03	47.7	6.2	13.0
37	3.0	103	12.0	41.8	30.0	72.0
38	8.0	105	24.0	51.5	47.3	92.0
39	6.0	108	60.0	71.0	64.1	90.2

TABLE VIII

REACTION OF MALEIC ACID IN NON-AQUEOUS MEDIUM (METHYL ETHYL KETONE) AT 80°C

(550 cc maleic acid solution/40 gms. asbestos. Acid equivalent data below are per formula weight of asbestos-554. Initial concentration of acid on this basis-6.02 mols. Ref. No. 102LCS42.).

Reaction Time, Hrs.	Equivalents 1st H^+ (Methyl red indicator)	
	Unreacted	Reacted
0	6.02	0
17.25	5.68	0.34
41.75	5.33	0.69
65.75	5.08	0.94
89.75	5.07	0.95
113.75	5.07	0.95

Titrations with phenolphthalein compared with methyl red indicated practically no 2nd H^+ reaction. Analysis of water soluble portion of residue from reaction indicated 0.34 atoms of Mg/formula weight of asbestos solubilized as magnesium salt.

TABLE IX

REACTION OF ASBESTOS IN NON-AQUEOUS MEDIUM (CYCLOHEXANONE) AT 140°C.

(700 cc. of maleic acid solution/40 gms. asbestos, Acid equivalent data below are per formula weight of asbestos-554. Initial concentration of acid on this basis-5.77 mols.)

Reaction Time, Hrs.	Equivalent 1st and 2nd H^+ (Phenolphthalein indicator) Unreacted	Reacted
0	5.77	0
2.17	4.85	0.82
7.17	4.64	1.03
13.17	4.65	1.02

Titrations with methyl red indicator were not sharp in this instance so that differentiation of reaction of 1st H^+ and 2nd H^+ was not obtained.

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