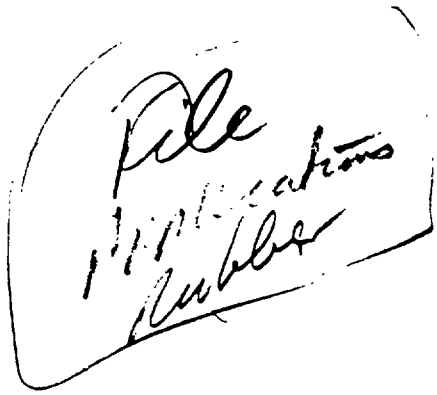
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PROJECT REPORT



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ORGANIC ELASTOMERS

UTILITY OF INTERFACIAL COUPLING AGENTS FOR ASBESTOS REINFORCED ELASTOMERS

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PLAINTIFF'S EXHIBIT
UC-380

SUMMARY

The program initiated to extend the concept of phenolic interfacial coupling agents in asbestos filled thermoplastics to that of elastomers was augmented by the inclusion of a silane treated asbestos. The results in both respects are encouraging in that a positive coupling of the asbestos to the rubber backbone appears to have taken place. As far as can be determined, this is the first time an effective coupling has been achieved between asbestos and a rubber polymer. While considerable work must be done to determine the feasibility of market penetration, the results encourage the recommendation to extend the investigation of interfacial coupling agents for asbestos in elastomers.

UNION CARBIDE CORPORATION – CHEMICALS AND PLASTICS
RESEARCH AND DEVELOPMENT DEPARTMENT
TARRYTOWN, NEW YORK

INTRODUCTION

CALIDRIA HPP and HPO (high purity pellets and high purity open) asbestos for rubber have been marketed over the past three years by the UCC distributor, Harwick Chemical Corp., Akron, Ohio. Work done at Tarrytown had shown the superiority of CALIDRIA high purity material over the conventional Canadian (Grade 7) asbestos. This effort was finalized by the issuance of the advertising booklet (F-70-081) which provided the rubber industry with formulations and physical data substantiating CALIDRIA asbestos as a reinforcing filler in elastomers.

The superiority of CALIDRIA asbestos over the conventional type is due to the following features:

1. Purity is $> 97\%$. Canadian asbestos is 40-60% pure - the remaining material being ground rock that imparts a degrading effect to a rubber matrix.

2. Magnetite (Fe_3O_4) content is $< 0.7\%$. As Fe^{+++} is a cause of reversion at heat age temperatures, especially in unsaturated polymers, the heat stability of CALIDRIA asbestos reinforced rubber is optimum.

3. Adequate surface area of 60 m^2/gm.

4. Controlled pH (2% slurry in H_2O) of 9, allowing for more flexibility in curing mechanisms.

5. High oil (DOP) absorption of 120 lbs./100 lbs.

6. High aspect ratio of 200:1.

While all of the above serve to characterize an optimum filler for rubber, the anisotropic effect of the high aspect ratio (item 6) works in divergent ways. From a positive viewpoint, it allows for high 90° to grain tear values by providing a migration barrier due to the filler ratio of length to diameter. The negative effect is observed in high set at break and permanent set, medium compression set and heat distortion resistance. As the filler loadings when using asbestos are usually high, it is theorized that the 200:1 aspect ratio results in a high degree of grain orientation by the filler during stress. While this works positively in some stress-strain functions, it does result in inadequate matrix memory. Unlike spherical fillers (or ones with a low aspect ratio), the tube configuration of the asbestos fibril does not allow the particulate to return in the same path after break, but most probably results in a canting within the vacuole created around the filler-polymer interface. The cumulative effect of this phenomenon when high filler loadings are involved is evidently greater than the "return spring" effect imparted to the matrix by optimum cross-linking and physical memory of the elastomer molecules. This would block the memory of the rubber mass. As it is well documented that bonding of a silica filler to a polymer reduces the above deficiencies to our acceptable level, it has been postulated that interfacial coupling of the asbestos surface to an elastomer would work in the same manner.

Interfacial coupling of CALIDRIA to polar and non-polar elastomers was investigated via the silane addition route in 1971. At this time, A-189 (gamma-mercaptopropyltrimethoxy silane) and A-100 (gamma-aminopropyltriethoxy silane) were added "in situ" to the asbestos during Banbury mixing. As the chemical composition of CALIDRIA asbestos is $Mg_3Si_2O_5(OH)_4$, sufficient ~Si-O-Mg-OH should be exposed along the surface of the 5μ x .025μ tube to react with the silane alkoxy groups. The organofunctional groups would be expected to bond to the elastomer backbone during curing. Physical results of the silane treated trial were only marginally increased over the control. It was apparent that the silane addition produced an inadequate filler-coupling agent bond due to the brucite (~MgOH) surface of the asbestos.

The advent of alkyl phenolic interfacial agents for asbestos-filled polyolefins (Project Reports File Nos. 3365 and 3427 by R. G. Azrak and F. H. Ancker) and the improvements in physical properties reported suggested that this might be a viable route to go in asbestos-filled elastomers. During the phenolic coupling agent investigations in rubber, a new approach to silane treatment of asbestos was made known. Acid leached HPO asbestos (ALX), in which the brucite surface was removed, was supplied by R. G. Woolery of Niagara Falls Metals and Mining R&D. This material was treated with A-189 silane by S. E. Berger and submitted for inclusion in the asbestos trials. The results of these recent investigations are covered in the Discussion section of this report.

DISCUSSION

The initial work utilizing the concept of phenolic coupling agents in rubber involved the use of RG-600 (dimethylol tertiary-butyl phenol treated HPO asbestos) as well as an "in situ" DMTBP treatment of HPO asbestos in both EPDM and NR using peroxide free radical and ionic sulfur and mixed free radical sulfur mechanisms. The presence of a t-butyl tail in the para position would be expected to block a coupling agent reaction to the elastomer backbone (Figure 1). It was important, however, at the start of this investigation to determine the overall effect of the treated asbestos versus untreated HPO on various rubber matrices to develop a base line. The object was to see if there were any differences in overall reinforcement of the asbestos in rubber due to the chemically altered surface of the experimental filler (Figure 1).

Table I shows the results of the initial investigation in EPDM and NR using varying types and amounts of filler combinations and curing mechanisms. Columns 1, 3, 5, 7, 9 and 11 are controls and 13 and 14 represent an "in situ" Banbury addition of DMTBP syrup to arithmetically equal the phenolic specie pretreated on RG-600. In general, there is a decrease in the reinforcing response when RG-600 is used versus HPO. It is evident that the control filler/polymer relationship has been downgraded by the use of RG-600. Assuming a monomolecular layer of DMTBP, as portrayed in Figure 1, normally reactive filler surface sites (actual interaction has not been defined) would be rendered chemically inactive and/or stearically hindered. If, on the other hand, the DMTBP/filler interface would be expected to impart a more positive relationship to the backbone, the effects of this have been nullified by the presence of the non-reactive t-butyl tail.

Extension of this initial work was made by the use of magnesium oxide and hexamethylene tetramine inclusions (Table II). As it was not known whether the DMTBP had been fully advanced during the pretreatment steps in making RG-600, the use of MgO would tend to complex the resin and hexa would provide a source of methylene groups. The net effect would be analogous to that seen in two-step thermosetting phenolic resins in rubber with the predictable shift in physical properties. No significant results were obtained as indicated on Table II.

At a review of the work to date with F. Ancker and M. Bertolucci, it was pointed out that the use of an RG-600 type material would not give the desired coupling effects in a rubber matrix with the consequent increases in physical properties. Based on the successes of this concept in asbestos reinforced polyolefins, it was decided to replace the non-reactive t-butyl site with an active one. Dimethylol isopropyl phenol (DMIPP) was chosen as the isopropyl tail would provide an active hydrogen for interaction with the elastomer backbone. While this site is not ideal in a sulfur mechanism, facile of synthesis would provide material for a trial using a thiazole/accelerated sulfur crosslinking system. The data presented on Table III show the shift in 300% modulus obtained. While this is far from ideal, considering the effects desired, it is felt that the EPDM results indicate a trend towards a low order filler-coupling agent-elastomer interaction. Had project time permitted, it is felt that the use of a peroxide free radical crosslinking system (DiCup 40C accelerated with SR-350, see subnotes on Table I) would show a marked improvement due to the reaction of a peroxide free radical with the active hydrogen on DMIPP. This step does, however, point out the need for organofunctionality more amenable to sulfur curing systems to provide a broad base. In this respect, the use of a mercapto ~~SH or a disulfide ~~S-S~~, the latter involving two phenolic groups, would provide the necessary mechanisms.

The second phase of the work on interfacial coupling agents for asbestos in elastomers involved the use of the acid leached (ALX) HPO asbestos which had been pretreated with A-189. As stated earlier in this report, the removal of the brucite (~~MgOH) from the asbestos resulted in an ~~SiOH surface which would react hydrolytically with the alkoxy groups on the silane coupling agent, resulting in an ~Si-O-Si asbestos/A-189 interface (Figure 2).

The formulations shown on Table IV include the use of ALX asbestos to again determine a base line for comparison of straight HPO and the silane treated material. The thiazole/accelerator system has not been optimized for a silane study of this nature nor had any attempt been made to determine the optimum loading of silane on the filler. Mr. S. E. Berger's carbon analysis reports indicated ~ 3.5% A-189 addition.

The physical results on Table IV (columns 1 vs. 3 and 4 vs. 6) indicate a definite response to the silane treated asbestos. The upward shift of the modulus curve indicates that a filler/elastomer coupling has been achieved. The most dramatic results are in the 5X drop in Set at Break. Taking these data to a logical conclusion, one could predict that the sought after decrease

in compression set and permanent set, as well as increased heat distortion resistance, may be achieved via this route. The results in columns 2 and 5 versus their respective controls are better than one might expect from only an acid leached material. This can be explained by the differences in surface area. Standard HPO has a surface area of 60 m^2/gm. while the ALX has 160 m^2/gm. due to the removal of the brucite surface. There is no evidence of or chemical reason for a true coupling effect with ALX asbestos alone.

As of the writing of this report, sufficient ALX material has been received from R. G. Woolery's group for further A-189 (or other active sulfur silane) treatment. Project clearance permitting a study of the optimum silane volume on the filler using revised curing mechanisms consistent with balanced physical properties will be undertaken.

CONCLUSIONS

It is apparent from the investigation that an effective chemical bond is possible between asbestos and a rubber backbone via the use of interfacial coupling agents of the types described. As far as can be determined, this is the first time this has been done using these technologies. While considerable synthesis work on appropriate organofunctional (mercapto, disulfide or polysulfide) reaction sites for the phenolic specie along with development effort on the technological parameters of end-use applications of that specie as well as the silane treated asbestos are needed, it is recommended that this work be continued so that the cost/performance of optimized systems in rubber can be determined.

NOTEBOOK REFERENCES

1152 and addendums

PATENTABLE FEATURES

An invention letter has been written (72-15) per Project Report File No. 3427 (R. G. Azrak) covering the use of phenolic interfacial agents in asbestos reinforced thermoplastics. Extension of this use to include elastomers should be made when appropriate. Letter of M. W. Ranney to J. H. Lorenz dated August 13, 1974 indicated intention to file for patentability of silane treated asbestos by December 1, 1974.

D. D. Berry/R. V. Girardi:et

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R. V. Girardi et

DATE WRITTEN: October 4, 1974

DATE APPROVED: October 11, 1974

DATE TYPED: October 16, 1974

Union Carbide trial exhibit UC-380: D. D. Berry and R. V. Girardi, Project Report on Interfacial Coupling Agents for...
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TABLE I

Evaluation of RG-600 (DMTBP) Asbestos In EPDM And NR

Ingredients (PPHR)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Vistalon 6505	100	100	100	100	100	100	-	-	-	-	-	-	-	-
SMR - 5L	-	-	-	-	-	-	100	100	100	100	100	100	100	100
SRF-HM Black	20	20	20	20	-	-	-	-	-	-	-	-	-	-
MT Black	-	-	-	-	-	-	20	20	-	-	-	-	20	-
Hi Sil 233	-	-	-	-	15	15	-	-	15	15	-	-	-	-
Calidria HPP Asbestos	65	-	65	-	50	-	65	-	50	-	65	-	65	65
RG-600 Asbestos	-	65	-	65	-	50	-	65	-	50	-	65	-	-
DMTBP Syrup (90%)	-	-	-	-	-	-	-	-	-	-	-	-	8	8
Stearic Acid	1	1	-	-	1	1	1	1	1	1	4	4	1	4
Zinc Oxide	5	5	-	-	5	5	5	5	5	5	5	5	5	5
Sulfur	1.5	1.5	-	-	1.5	1.5	1.5	1.5	1.5	1.5	2.5	2.5	1.5	2.5
MBT (1)	0.5	0.5	-	-	0.5	0.5	0.5	0.5	0.5	0.5	-	-	0.5	-
TMTD (2)	1.5	1.5	-	-	1.5	1.5	1.5	1.5	1.5	1.5	-	-	1.5	-
Altax (3)	-	-	-	-	-	-	-	-	-	-	0.7	0.7	-	0.7
DPG (4)	-	-	-	-	-	-	-	-	-	-	0.3	0.3	-	0.3
Di Cup 40C (5)	-	-	5	5	-	-	-	-	-	-	-	-	-	-
SR-350 (6)	-	-	4	4	-	-	-	-	-	-	-	-	-	-
M/B Mooney Viscosity (MS 1 + 4 @ 250°F)	83	63	54	79	72	83	80	80	69	70	58	36	31	32
F/M Mooney Scorch T_5 MS 1 @ 250° F	2.5	6.5	2.0	6.5	4.0	7.5	2.5	2.5	3.0	3.0	5.0	10.0	2.5	7.5
Monsanto ODR (1° - 3 OPM - 320°F)														
T_{90} (Min.)	21.5	10.0	12.0	17.0	26.0	22.0	2.0	1.0	2.0	1.5	4.5	7.0	1.0	13.0
CRI	4.8	11.4	8.7	6.6	4.0	5.1	66.7	200	100	200	28.6	18.2	100	8.9
Mold Cure (Min. @ 320°F)	22	10	12	17	26	22	5	5	5	5	8	11	5	13
Physical Properties														
Hardness, Shore A	89	84	87	83	89	83	85	80	82	78	74	72	81	80
Tensile PSI	2420	2380	2020	2200	1780	2040	2680	2420	3000	3010	1630	1270	2150	1770
Elongation, %	270	420	200	450	360	390	240	390	300	420	280	410	380	270
100% Modulus, PSI	1880	670	1590	660	1260	880	1880	800	1880	1010	860	450	590	1005
200% Modulus, PSI	2250	700	2020	870	1470	1080	2520	1010	2560	1370	1200	550	910	1505
300% Modulus, PSI	-	1080	-	1180	1630	1400	-	1780	3000	1980	-	770	1575	-
Tear "C" (With Grain), PPLI	450	330	400	350	420	390	370	350	410	370	330	210	250	280
Tear "C" (Against Grain), PPLI	500	290	390	340	420	360	300	330	360	330	300	210	-	-
Set At Break, %	80	90	60	100	80	110	65	85	85	105	70	105	90	70

(1) 2-Mercapto Benzothiazole
(2) Tetramethyl Thiuram Disulfide
(3) Benzothiazyl Disulfide
(4) Diphenyl Guanidine
(5) Dicumyl Peroxide (40% on Ca CO_3)
(6) Trimethylol Propane Trimethacrylate

✓ = Control

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TABLE II

Evaluation of RG-600 (DMTBP) Asbestos In EPDM

Incorporation Of MgO And Hexamethylene Tetramine

Ingredients (PPHR)	1A	1B	2A	2B	5A	5B	6A	6B
Vistalon 6505	100	100	100	100	100	100	100	100
SRF-HM Black	20	20	20	20	-	-	-	-
Hi Sil 233	-	-	-	-	15	15	15	15
Calidria HPP Asbestos	65	65	-	-	50	50	-	-
RG-600 Asbestos	-	-	65	65	-	-	50	50
Stearic Acid	1	1	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5	5	5
Hexamethylene Tetramine	3	3	3	3	3	3	3	3
Magnesium Oxide	-	2	-	2	-	2	-	2
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Monsanto ODR								
(1° - 100 OPM-320°F)								
T_{90} (Min.)	16.5	14.0	11.0	17.0	19.0	20.0	14.0	17.0
CRI	6.7	8.0	10.8	6.5	5.8	5.4	8.3	6.7
Mold Cure (Min. @ 320°F)	15	15	11	18	18	18	15	18
Physical Properties								
Hardness, Shore A	83	83	86	86	83	83	83	84
Tensile, PSI	1870	2220	1970	2060	2275	2320	2100	2480
Elongation, %	350	520	390	420	455	490	410	470
100% Modulus, PSI	830	680	560	670	565	650	625	620
200% Modulus, PSI	1065	935	750	900	700	845	760	860
300% Modulus, PSI	1525	1160	1170	1230	1000	1095	1180	1160
Tear "C" (With Grain), PPLI	294	284	250	279	230	292	255	304
Set At Break, %	80	120	80	80	100	100	80	80

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TABLE III

Evaluation of DMIPP(1) Treated Asbestos In EPDM and NR

Ingredients (PPHR)	1	2	3	4
Vistalon 6505	100	100	-	-
SMR-H5L	-	-	100	100
SRF-HM Black	20	20	-	-
MT Black	-	-	20	20
Calidria HPO Asbestos	65	-	65	-
DMIPP Treated Asbestos	-	65	-	65
Stearic Acid	1	1	1	1
Zinc Oxide	5	5	5	5
Sulfur	1.5	1.5	1.5	1.5
MBT	0.5	0.5	0.5	0.5
TMTD	1.5	1.5	1.5	1.5
M/B Mooney Viscosity (MS 1 + 4 @ 250°F)	64	90	68	76
F/M Mooney Scorch T_5 MS 1 @ 250°F)	2.8	5.9	2.0	2.9
Mold Cure (Min. @ 320°F)	19	19	5	5
Physical Properties				
Hardness, Shore A	85	84	79	80
Tensile, PSI	2355	2390	2670	2380
Elongation, %	360	320	290	390
100%)	1070	825	1540	1200
200% } Modulus, PSI	1510	1240	2135	1550
300%)	1955	2250	-	2000
Tear "C", PPLI	360	320	340	340
Set At Break, %	110	70	90	90

(1) Dimethylol Isopropyl Phenol

TABLE IV

Evaluation of A-189 Treated Asbestos In EPDM and NR

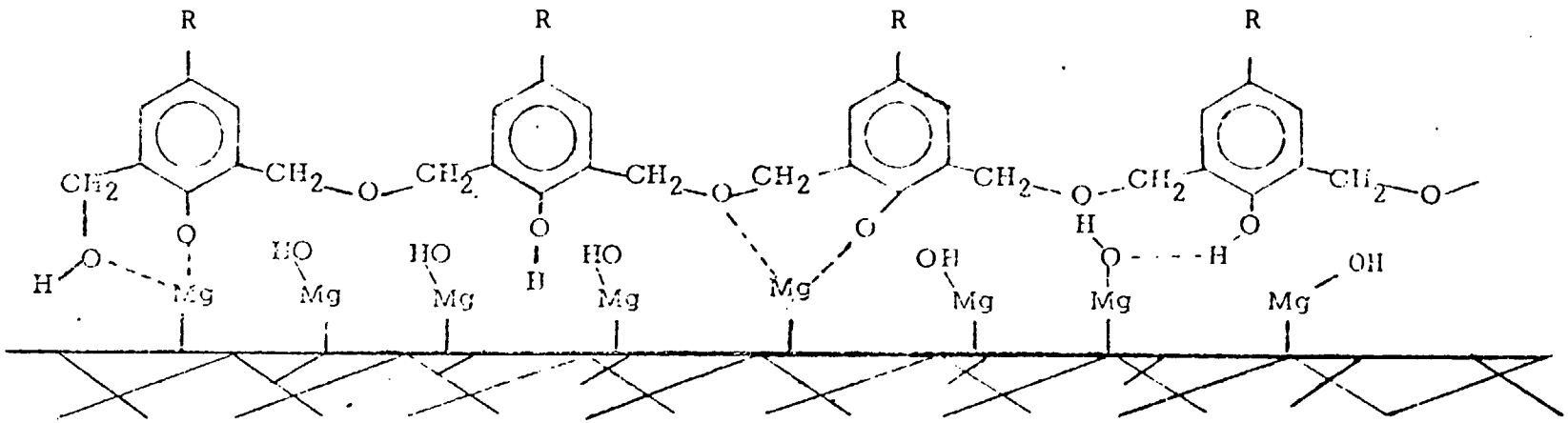
Ingredients (PPHR)	1	2	3	4	5	6
Vistalon 6505	100	100	100	-	-	-
SMR-H5L	-	-	-	100	100	100
SRF-HM Black	20	20	20	-	-	-
MT Black	-	-	-	20	20	20
Calidria HPO Asbestos	65	-	-	65	-	-
Calidria HPO Asbestos (ALX) (1)	-	65	-	-	65	-
Calidria HPO Asbestos (ALX) With A-189	-	-	65	-	-	65
Stearic Acid	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
MBT	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	1.5	1.5	1.5	1.5	1.5	1.5
M/B Mooney Viscosity (MS 1 + 4 @ 250° F)	59	84	86	34	35	34
F/M Mooney Scorch (T_5 MS 1 @ 250° F)	2.5	2.8	3.2	1.9	1.7	1.7
Mold Cure (Min. @ 320°F)	14	16	14	5	5	5
Physical Properties						
Hardness Shore A	85	86	86	79	80	81
Tensile, PSI	2200	1580	1900	2450	2300	2750
Elongation, %	430	400	200	310	250	160
100% Modulus, PSI	1065	1055	1480	1130	1390	2240
200% Modulus, PSI	1320	1260	1900	1600	1825	-
300% Modulus, PSI	1660	1475	-	2355	-	-
Tear "C", PPLI	360	340	350	330	300	300
Set At Break, %	110	100	25	100	60	20

(1) Acid Leached Experimental

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FIGURE 1

IDEALIZED SCHEMATIC OF POSSIBLE PHENOLIC/ASBESTOS SURFACE INTERACTIONS



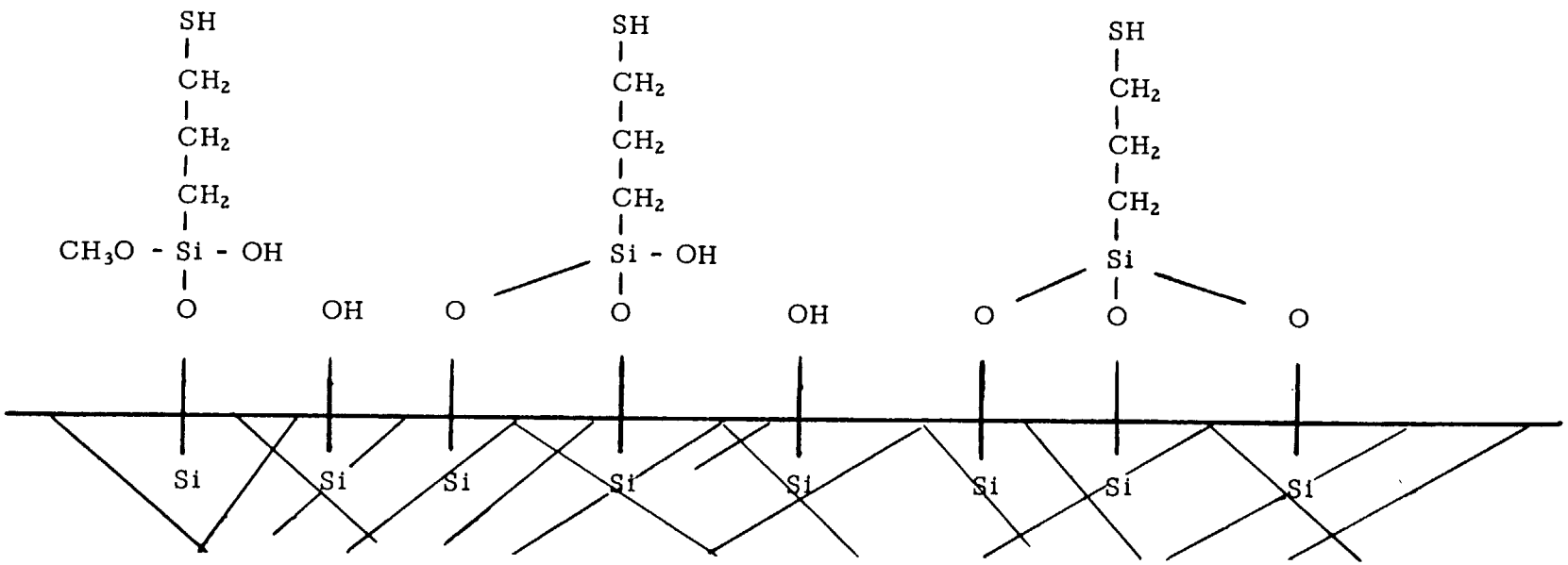
R = t-butyl or isopropyl

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FIGURE 2

IDEALIZED SCHEMATIC OF A-189/(ALX) ASBESTOS SURFACE INTERACTIONS



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