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PROJECT REPORT

PLAINTIFF'S EXHIBIT UC-382

CELLULAR AND ELASTOMER MATERIALS

UTILITY OF PHENOLIC INTERFACIAL COUPLING AGENTS FOR ASBESTOS REINFORCED ELASTOMERS

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SUMMARY

The extension of the concept of phenolic interfacial coupling agents in asbestos filled thermoplastics to that of elastomers has, with the synthesis of increasingly reactive thiophenolic monomers, resulted in an apparent reinforcement between the asbestos and the rubber backbone. Increases in the stress-strain characteristics of the test samples and corresponding decreases in deformation set indicate that the filler/polymer relationship has been enhanced via chemical bonding at the interfaces. It is believed that this is the first time this phenomenon has been documented between asbestos, treated as above, and a rubber polymer.

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UNION CARBIDE CORPORATION – CHEMICALS AND PLASTICS

RESEARCH AND DEVELOPMENT DEPARTMENT

TARRYTOWN, NEW YORK

INTRODUCTION

The background leading up to the data presented in the body of this report was delineated in a previous Project Report, i.e. "Utility of Interfacial Coupling Agents for Asbestos Reinforced Elastomers", File No. P-74-177. The history of the use of CALIDRIA HPP and HPO (high purity pellets and high purity open) asbestos in elastomers was detailed as were the results of various investigations into the area of asbestos/rubber polymer coupling via the use of phenolic monomers on the filler surface.

The reasoning leading to the objective to couple asbestos to a rubber backbone was prompted by a definite physical need plus the prior work of R. G. Azrak and R. H. Ancker (Bound Brook R&D Project Reports File Nos. 3365 and 3427) on the use of alkyl phenolic interfacial agents for asbestos filled polyolefins. In the need category, even though it had been shown that CALIDRIA Asbestos is characterized as a semireinforcer, its use resulted in poor deformation and set resistance, primarily due to its aspect ratio of 200:1 (5μ x .025μ tubular fibril).

The work completed first involved the use of CALIDRIA Asbestos RG-600. This material was pretreated with 10 wt. % of dimethylol tertiary-butyl phenol and had been successfully used in asbestos-filled polyolefins. The presence of an unreactive (to sulfur curing mechanisms) t-butyl tail not only precluded coupling but, in fact, nullified normally reactive filler surface sites available on non-treated asbestos and gave poorer physical properties than the HPP controls. Assuming a viable surface interaction between the asbestos and the DMTBP, it became apparent that the t-butyl tail should be replaced by a more reactive site. It was decided that for facile of synthesis, dimethylol isopropyl phenol (DMIPP) would be used to provide an active hydrogen for rubber backbone interaction. While this site is not ideal in a sulfur mechanism, a definite trend towards upgrading the stress-strain characteristics of the matrices was noted. The next logical step would be the utility of an organofunctional site amenable to ionic sulfur curing systems. This step was finalized by M. S. Leung and F. H. Ancker, Bound Brook R&D, via the preparation of two thiofunctional monomers, 2,6-dimethylol-4-mercaptophenol (DMMP) and 4,4'-bis (2,6 dimethylol phenol) disulfide (b-DMPD). The synthesis and identification of these monomers are shown in Figures 1 and 2 (letter MSL to DDB 2/23/76). Sufficient quantities of RG-144 asbestos were treated to 10 wt. % level and sent to Tarrytown for the trials reported on at this time.

DISCUSSION

In the interest of chemical coupling of an inorganic filler to an elastomer macropolymer, two basic reactions must be accomplished. One is a positive reaction between the interfacial agent and the filler, and the other a positive reaction between the coupler and the elastomer. It had been demonstrated that the former was a reality (Azrak and Ancker Project Reports File Nos. 3365 and 3427) with a 2,6 dimethylol phenol treatment to RG-144 asbestos as indicated by the schematic shown on Figure 3. As previous work in sulfur crosslinked elastomeric formulations had shown, the latter reaction should be viable if

reactive sulfur sites were made available on the para position of the 2, 6 dimethylol phenol. This rationale resulted in R substitution (Figure 3) of ~SH and ~S-S~.

An interesting point to consider at this time is that while the DMMP treated asbestos can be visualized by Figure 3, the b-DMPD treated material would most likely be a mirror image of asbestos/phenolic interfacial agent/ asbestos due to the bis structure of the phenolic monomer. If this is the case, one could predict a higher degree of reinforcement from the b-DMPD as both monomer loadings were 10 wt. %. This will be shown further on in this report.

The formulations used in this trial were identical to those of previous efforts. EPDM, due to its saturated backbone with minimal pendant unsaturated crosslinking sites, and the highly backbone unsaturated cis-polyisoprene were used. The curing mechanisms were of the standard thiazole /thiuram (2-mercapto benzothiazole/tetramethyl thiuram disulfide) type to accommodate the mercapto functional phenol and the disulfide/amine (benzothiazyl disulfide/ diphenyl guanidine) type more amenable to optimum reaction with the bis-thio phenol. For brevity and simplicity, only the DMMP treated asbestos/unsaturated backbone elastomer interaction is shown on Figure 4. Here, the objective of reacting the mercapto functional phenol is shown via allylic insertion to the elastomer. This would proceed along the same lines as the curing system used in that the mercaptan will react with soluble zinc stearate in the formulations used to yield the zinc mercaptan salt. The zinc is split off as zinc sulfide during a further reaction with elemental sulfur in the formulation and insertion will take place with an asbestos/phenolic/elastomer relationship established. In the case of the b-DMPD treated asbestos, the same sequence would be involved after reductive fission of the disulfide phenol, again along the same lines as the curing system indicated.

The EPDM and NR trial data are shown in Tables I and II. The results of asbestos/elastomer coupling can be seen in columns 1, 2, 3 and 4 when compared to the appropriate controls. The objectives of (1) increased stress-strain characteristics, and (2) decreased set have been met. To those not desiring to review property for property on these tables, a recapitulation of the salient points is made in Table III. The higher increases in stress-strain values in the b-DMPD work, columns 2 and 4, are attributable to two causes: (1) the potential presence of more reactive coupling sites due to the bis structure, and (2) the normal slower curing tendencies of a ~S-S~ mechanism resulting in the formation of high bond energy mono-thio ether linkages. This is , however, a plus value, as the "state of the art" is replete with the means to decrease the cure time and increase the efficiency of disulfide systems without drastically reducing their main processing point, i.e. long scorch time. The corresponding decreases in set at break of all the trials shown on Table III are cause for consideration. It is here that we see the effects of a coupled system and, therefore, a tighter matrix. The reduction of set to acceptable levels of 15 to 30% for EPDM and 10 to 30% for NR, depending on the curing system and coupling agent used, is a decisive accomplishment.

CONCLUSIONS AND RECOMMENDATIONS

The use of a phenolic interfacial agent to couple asbestos filler to an elastomer backbone has been proven viable within the context of this report via both mercapto (DMMP) and disulfide (b-DMPD) functional dimethylol phenol. As far as can be determined, this is unique and patentable. As the formulations used are designed only to show the "goodness" of the concept in a weak (EPDM) system and a strong (NR) system, there remains considerable work to be done in "fine tuning" the formulations and curing systems on an applied basis and determining the optimum amount of coupling agent needed to achieve specific objectives.

In addition, the market potential would require definition in terms of cost/performance of optimized systems in rubber. Further R&D work would be applied along the following lines commensurate with the requirements of market penetration.

1. Determine the finite amounts of coupling agent required for optimum results.

2. Determine the overall efficiency from both a processing and coupling standpoint of a mercapto versus a disulfide system.

3. Determine the feasibility of balanced mol. % "in situ" addition of the coupling agent versus pretreatment.

4. In the case of the disulfide moiety, determine the effects of the presence of ~C-S-S-C~ versus ~C-S-S_x-S-C~ structures (x = 1, 2 or 3).

5. Investigate the overall effects of reactive phenolic sulfur sites on the standard curing mechanisms used to determine the real and absolute contributions of the interfacial agents to the increased physical properties. The curing systems would be optimized via this probe.

6. Determine the effects on heat age and dynamic environmental properties contributed by the phenolic moieties.

NOTEBOOK REFERENCES

2581, pp. 49-55 and addenda

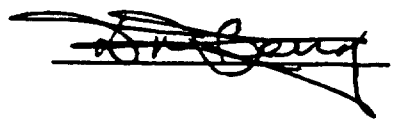
PATENTABLE FEATURES

Applications for patents on material contained in this report will be referred to the Legal Department when appropriate.

ACKNOWLEDGEMENTS

Appreciation is extended to M. S. Leung, Bound Brook R&D, for synthesis of the phenolic coupling agents and preparation of the treated asbestos, and to R. V. Girardi, Tarrytown R& D, for the formulation, curing and testing work involved.

D. D. Berry/et



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TABLE I

EVALUATION OF DMMP AND b-DMPD TREATED ASBESTOS IN EPDM

Ingredients (PPHR)	Control 1	1	Control 2	2
"Vistalon" 6505[1]	100	100	100	100
SRF-HM Black[2]	20	20	20	20
RG-144 Asbestos	65	-	65	-
DMMP Treated Asbestos	-	65	-	-
b-DMPD Treated Asbestos	-	-	-	65
Stearic Acid	1	1	2	2
Zinc Oxide	5	5	5	5
Sulfur	1.5	1.5	2.5	2.5
2-Mercapto Benzothiazole	0.5	0.5	-	-
Tetramethyl Thiuram Disulfide	1.5	1.5	-	-
Benzothiazyl Disulfide	-	-	0.7	0.7
Diphenyl Guanidine	-	-	0.3	0.3
M/B Mooney Viscosity (ML I + 4 @ 212°F)	155	178	140	162
F/M Mooney Scorch (T_5 MSI @ 250°F), min.	3.75	6.5	5.9	17.7
Monsanto ODR (1° - 1 OPM - 320°F)				
T_2, min.	1.5	1.5	1.75	3.0
T_{90}, min.	20	8.25	20	38.25
Mold Cure (min. @ 320°F)	20	9	20	39
Physical Properties				
Hardness, Shore A	84	83	81	81
Tensile, psi	2153	1920	1893	2006
Elongation, %	336	240	735	280
100 % Modulus, psi	1310	1581	545	1440
200 % Modulus, psi	1605	1830	627	1693
300 % Modulus, psi	1978	-	712	1819
Tear "C", ppli	221	192	250	209
Set at Break, %	80	15	150	30

(1) EPDM containing ~9 mole % ethylidene norbornene for sulfur crosslinking.
(2) Semireinforcing Furnace Black.

TABLE II

EVALUATION OF DMMP AND b-DMPD TREATED ASBESTOS IN NR

Ingredients (PPHR)	Control 3	3	Control 4	4
SMR-H5 (1)	100	100	100	100
MT Black (2)	20	20	20	20
RG-144 Asbestos	65	-	65	-
DMMP Treated Asbestos	-	65	-	-
b-DMPD Treated Asbestos	-	-	-	65
Stearic Acid	1	1	3	3
Zinc Oxide	5	5	5	5
Sulfur	1.5	1.5	2.5	2.5
2-Mercapto Benzothiazole	0.5	0.5	-	-
Tetramethyl Thiuram Disulfide	1.5	1.5	-	-
Benzothiazyl Disulfide	-	-	0.7	0.7
Diphenyl Guanidine	-	-	0.3	0.3
M/B Mooney Viscosity (MLI + 4 @ 212°F)	118	88	94	85
F/M Mooney Scorch (T_5 MSI @ 250°F), min.	3.05	3.55	6.3	17.6
Monsanto ODR (1° - 1 OPM - 320°F)				
T_2, min.	1.5	1.25	1.25	2.5
T_{90}, min.	2	2	4.25	9.5
Mold Cure (min. @ 320°F)	2	2	4.5	10
Physical Properties				
Hardness, Shore A	80	78	77	75
Tensile, psi	2682	2479	2191	2418
Elongation, %	245	160	317	226
100 % Modulus, psi	1877	2089	912	1480
200 % Modulus, psi	2544	-	1340	2242
300 % Modulus, psi	-	-	1945	-
Tear "C", ppli	325	260	195	156
Set at Break, %	70	10	90	30

(1) Natural cis-polyisoprene
(2) Medium Thermal Black

TABLE III

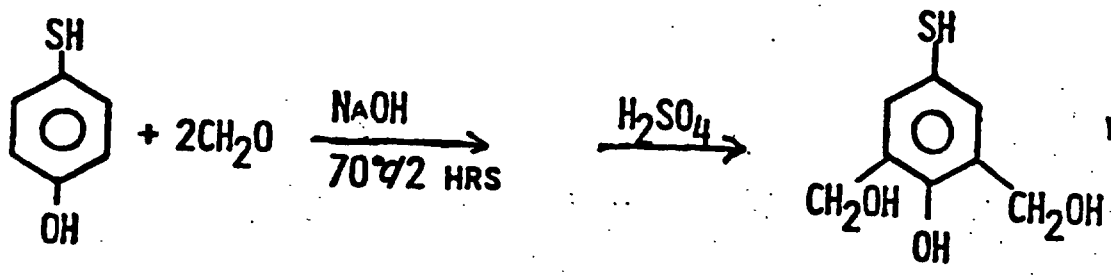
MODULUS AND SET AT BREAK RECAPITULATION

OF TABLES I AND II

	EPDM		NR	
	DMMP	b-DMPD	DMMP	b-DMPD
	1	2	3	4
100 % Modulus Increase, %	21	164	11	62
200 % Modulus Increase, %	14	170	-	67
300 % Modulus Increase, %	-	155	-	-
Set at Break Decrease, %	433	400	600	200

FIGURE 1

SYNTHESIS AND IDENTIFICATION OF DMMP



FROM ~75%

ELEMENTAL ANALYSIS

	CALC.	FOUND
C	51.6	51.5
H	5.4	5.8
O	25.8	26.6
S	17.2	16.1

NMR

CH_2-OH AT 2,6 POSITION CONFIRMED BY C-13 NMR

CHEMICAL TEST

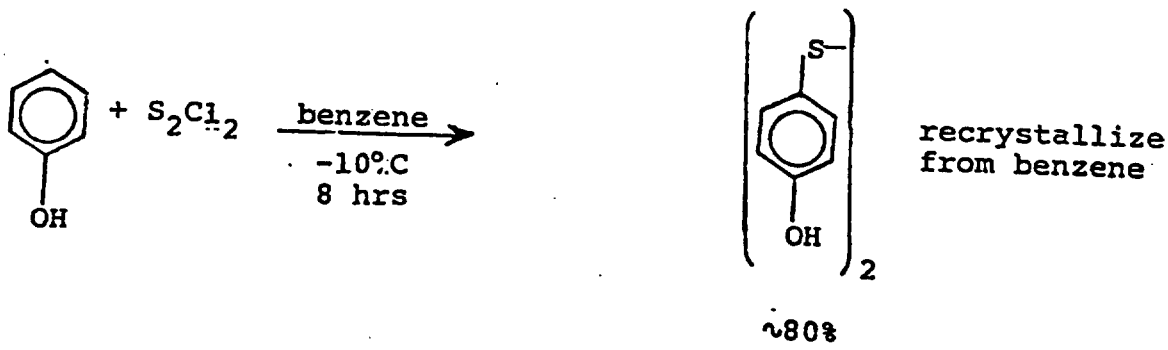
FOR -SH:
POSITIVE

PHYSICAL CHARACTERISTICS:

WHITE CRYSTALLINE SOLID
MELTING POINT: 155°C WITH POLYMERIZATION
INSOLUBLE IN METHANOL
SOLUBLE IN PYRIDINE
LITTLE ODOR

FIGURE 2

SYNTHESIS AND IDENTIFICATION OF DMPD



~80%

(Adopted from Arigan and Wiles, J. Chem. Soc. 3876 (1962))

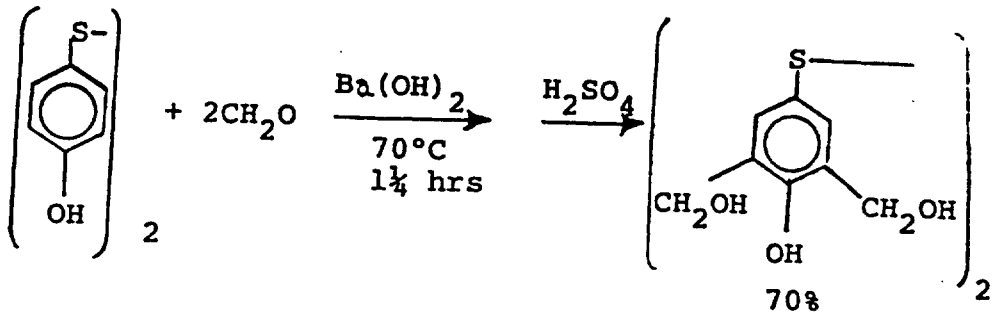
Elemental Analysis

	Calc.	found
C	57.5	57.7
H	4.0	4.0
O	12.8	12.5
S	25.7	25.8

NMR

-S-S-

at 4-4' position



70%

Elemental Analysis

	Calc.	Found
C	51.9	52.6
H	4.9	5.1
O	26.0	26.5
S	17.2	15.8

NMR

$-CH_2OH$

at 2,6 position
confirmed by
C-13 NMR

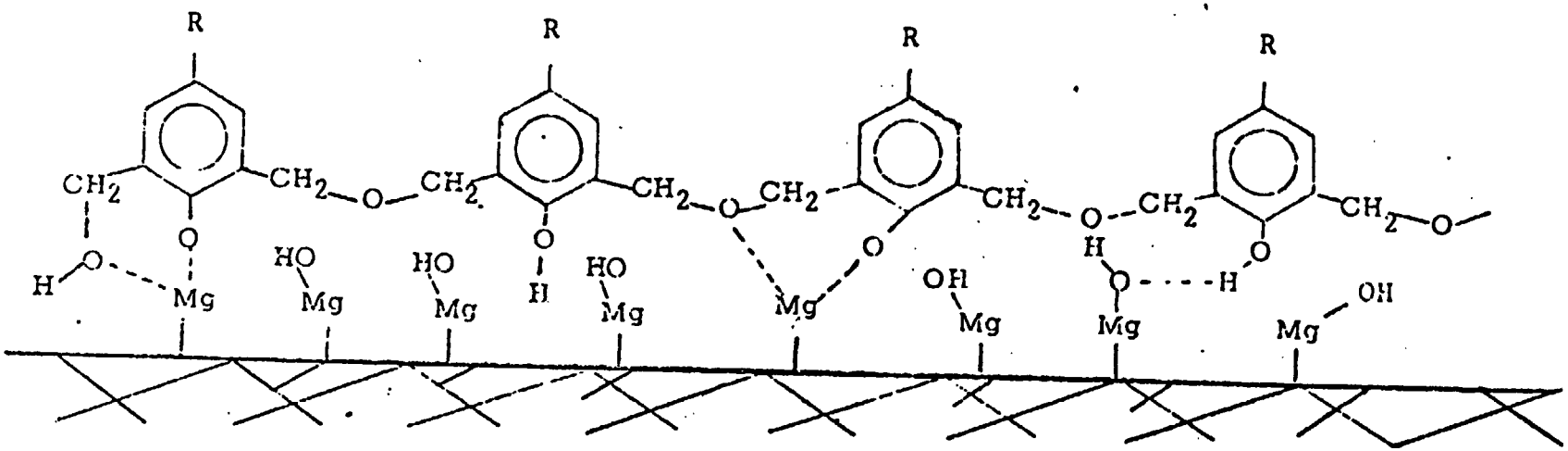
Physical Characteristics:

Yellow viscous liquid
soluble in both methanol and pyridine
little odor

Union Carbide trial exhibit UC-382: D. D. Berry Project Report on Phenolic Interfacial Coupling Agents for Asbesto...
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FIGURE 3

IDEALIZED SCHEMATIC OF POSSIBLE PHENOLIC/ASBESTOS SURFACE INTERACTIONS



R = -SH or -S-S-Bis-phenolic/asbestos.

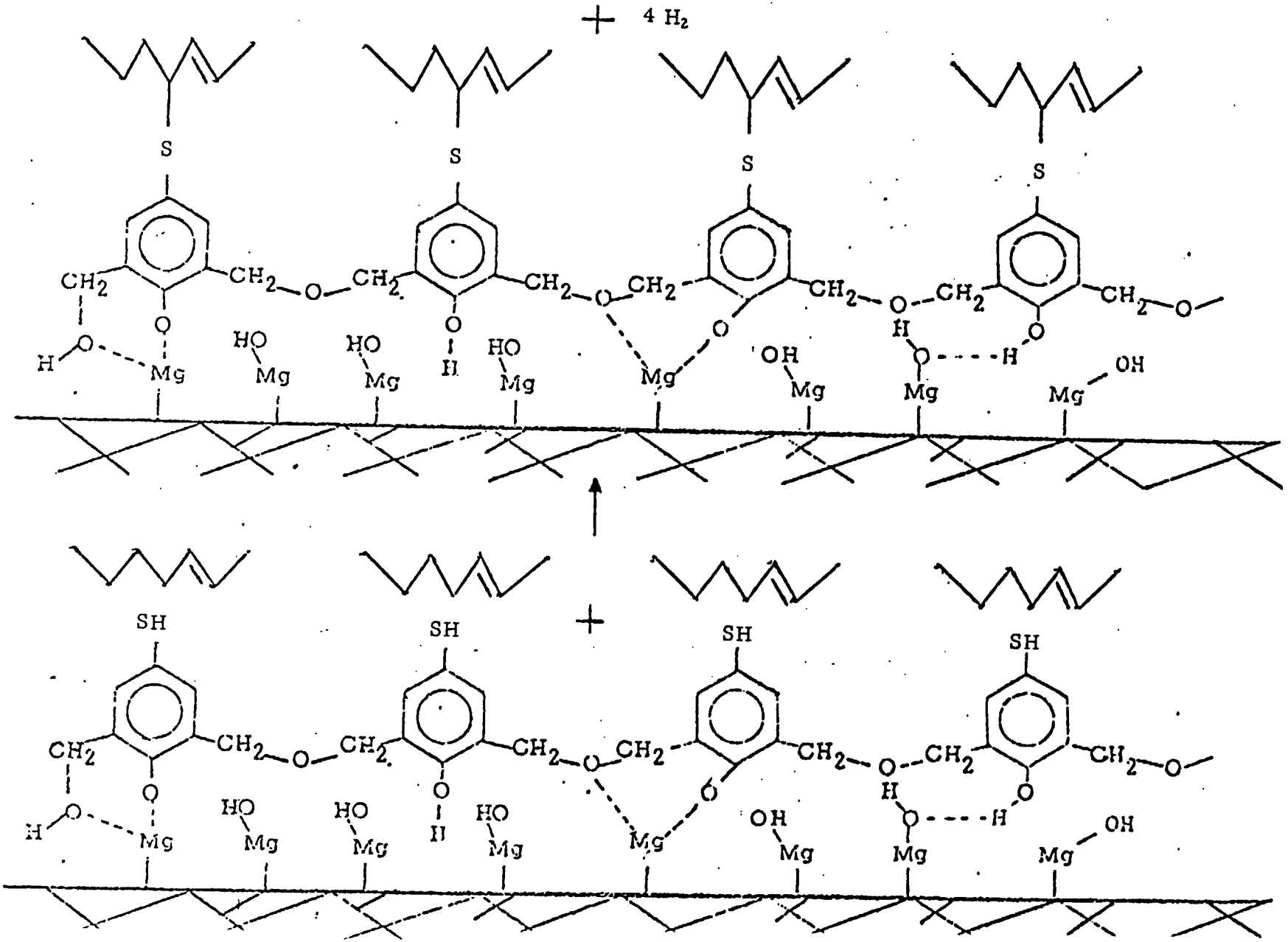
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FIGURE 4

IDEALIZED SCHEMATIC OF DMMP TREATED ASBESTOS/UNSATURATED ELASTOMER INTERACTION

IONIC MECHANISM - ALLYLIC INSERTION



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