WV-0001 #11

STATUS REPORT

NEW ENTERPRISES

CHEMICAL REACTIONS OF ASBESTOS

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SUMMARY Attempts to add asbestos to the double bond of activated vinyl compounds were unsuccessful; apparently, the necessary silanol groups are not present.

A 2 per cent addition of organic material to asbestos was achieved by heating a toluene solution of divinylspirobi-(m-dioxane) with asbestos. Sodium hydroxide catalysis, however, resulted in an 8.6 per cent organic loading which was identified as acrylate ion. The acrylate-modified asbestos is a light grey powder which is more easily obtained by direct reaction of asbestos and acrylic acid.

Uncatalyzed mesityl oxide and acrylonitrile do not react with asbestos at 100°. When a sodium hydroxide catalyzed cyanoethylation of asbestos was attempted, vinyl polymerization of acrylonitrile and adsorption of the polymer by asbestos took place. Mesityl oxide underwent an aldol condensation reaction exclusively on sodium hydroxide catalysis. The aldol polymer was physically adsorbed on asbestos.

The products of polymer adsorption on asbestos were colored, organophillic, hydrophobic solids which could be used as compatible resin fillers but which would result in discolored products.

INTRODUCTION The addition of chrysotile asbestos to activated vinyl compounds has been discussed previously in a report surveying the possible reactions of asbestos.(1)

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The formation of stable adducts from asbestos and vinyl compounds is dependent on the existence of weakly acidic silanol groups on asbestos:

$$\geqslant SiOH + CH_2{=}CHX \longrightarrow \geqslant Si\text{-}O\text{-}CH_2CH_2X$$

where X = -CN, $-CO_2R$, $-\overset{O}{\overset{\|}{C}}R$, $-\overset{O}{\overset{\|}{S}}R$, etc.

The theoretical structure of chrysotile currently favored does not contain silanol groups.

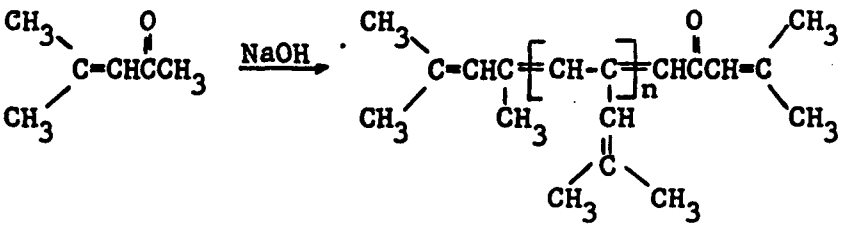
DISCUSSION Chrysotile asbestos, a weak base comparable in strength to magnesium hydroxide, should be sufficiently basic to catalyze the addition of silanol groups to activated carbon-carbon double bonds. Three compounds with activated vinyl groups were studied: mesityl oxide, acrylonitrile, and divinylspirobi(m-dioxane).

Without catalysis divinylspirobi(m-dioxane) in toluene reacted with asbestos to add less than 2 per cent organic material to asbestos. The product was not analyzed since a 2 per cent organic loading is insignificant. When 5 per cent powdered sodium hydroxide based on the divinylspirobi(m-dioxane) concentration was added, an 8.6 per cent organic loading was achieved. The product was identified as an asbestos acrylate salt by infrared analysis. A carbon-carbon double bond was indicated by an absorption band at 6.1μ, and a carboxylate salt by absorption bands at 6.22μ and 6.85μ. Some addition of asbestos to the activated double bond may have taken place but the principal reaction was salt formation:

$$CH_2{=}CHCH(O^-)(O^-) + \geqslant SiOMgOH \xrightarrow{NaOH} CH_2{=}CHCO_2^-\,{}^+MgOSi\leqslant$$

The reaction probably takes place by a base-catalyzed disproportionation similar to a Cannizzaro reaction but could also occur by air oxidation of the dioxolane as has been proposed for the formation of acrylate esters in air drying films from polymeric α-β-unsaturated dioxolanes[3] No attempt was made to isolate by-products.

Although uncatalyzed mesityl oxide failed to undergo any noticeable reaction with raw asbestos, the addition of powdered sodium hydroxide caused a vigorous exothermic reaction resulting in asbestos containing over 13 per cent red organic material. The base catalyzed aldol polymerization of mesityl oxide in water has been reported,[4] and the solid organic material extracted from the treated asbestos was easily identified at a higher aldol condensate by its color and infrared spectrum:

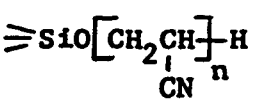


The existence of a conjugated double bond system was supported by the red color of the condensate (indicating a shift in absorption from ultraviolet to visible red light), by a conjugated carbonyl absorption band at 6.0μ and by an intense conjugated carbon-carbon double bond absorption band at 6.32μ. These bands compare with a carbonyl absorption band at 5.9μ and a carbon-carbon unsaturation band at 6.14μ for mesityl oxide.

Exhaustive reflux extraction of the product using different solvents (water, acetone, cyclohexanone) resulted in different organic loadings. The polymeric aldol condensates are probably low in molecular weight, C_{36}-C_{48}.[4]

Reproducible results were not obtained in the polyaldol condensation due to the heterogeneous catalyst.

Cyanoethylation of asbestos by heating an acetonitrile solution of acrylonitrile for 20 hours at 82° was unsuccessful. When the same procedure was repeated with a catalytic amount of powdered sodium hydroxide, polymerization took place. The product could be either a polymer grafted to asbestos:



or a polymer which is strongly adsorbed by asbestos because of the electron-accepting nitrile groups. A difference in organic loading (3GWR48) on asbestos samples exhaustively extracted with acetonitrile and dimethyl formamide indicates the organic polymer was physically adsorbed since the better solvent removed more material.

When the reaction was run with asbestos pre-fired at 1000° to remove hydroxyl groups, organic material was again added; this is further evidence of a physical adsorption of organic material. In this case (3GWR74), direct boiling in DMF was more effective in removing polyacrylonitrile than was Soxhlet extraction with DMF.

The DMF extractable portions of the organic material were a brown solid residue (polyacrylonitrile) which exhibited a nitrile band at 4.5μ.

CONCLUSIONS If silanol groups are present on chrysotile asbestos, they either exist in very small number or are unreactive toward cyanoethylation-type reactions.

Acrylate ion can be placed on the asbestos surface by a base catalyzed reaction of divinylspirobi(m-dioxane) and probably other acrolein acetals.

Asbestos modified by physically adsorbed polymers of mesityl oxide or acrylonitrile may exhibit increased compatibility[2] with organic resins, but no great increase in strength properties is to be expected over conventional filled resins.

No further work in the area of vinyl additions to asbestos is planned.

EXPERIMENTAL The asbestos, catalyst, and solvent were stirred as a thick slurry with ice water or brine cooling in a jacketed flash while the reagent was added at a rate such that the temperature was easily controlled. After any exotherm had subsided, the slurry was heated to the desired temperature and samples were pulled at the stated intervals. Reaction time was based on time at high temperature during both exotherm and external heating.

The solid product was filtered from the solvent and exhaustively extracted by the Soxhlet technique. After drying at 105° for 16 hours, the samples were ashed at 1000°C. and the weight loss was compared with the weight loss found with fired raw chrysotile asbestos (15.2 per cent).

REFERENCES

1. C. W. McGary and G. W. Rausch, "New Enterprises: Chemical Reactions of Asbestos," Formal Status Report, July 7, 1964, File No. 2746.

2. "Asbestos Data Book," page 12, Union Carbide Nuclear Division.

3. Carol K. Ikeda, U. S. 3,010,923, November 28, 1961.

4. Sumner H. McAllister and Vernon E. Haury, U. S. 2,309,650, February 2, 1943.

ATTACHMENTS: One table

Gerald Rausch

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eference	Reactant	Solvent	Wt. Reactant (1)	Wt. Asbestos (1)	Catalyst	Cat. Wt. (1)	Temp. (2)	Time (3)	Ext. Solvent	% Org. (4)
GWR28	Divinylspirobi-(m-dioxane)	250 ml. Toluene	290	60	--	--	100°	4	Toluene	1.6
								8		1.9
								12		1.9
GWR58	Divinylspirobi-(m-dioxane)	250 ml. Toluene	290	60	NaOH	14.5	100°	18	Toluene	8.1
GWR30	Mesityl oxide	Neat	400	60	--	--	120°	3	Acetone	0.6
								6		0.4
								9		0.4
								12		--
								15		1.0
								18		1.2
GWR62	Mesityl oxide	Neat	400	60	NaOH	20.0	100°	2.5	Acetone	13.5
									Water	13.5
GWR64	Mesityl oxide	Neat	400	60	NaOH	20.0	100°	0.5	Acetone	6.8
								3		6.6
								6		7.5
								10		9.3
								13		7.4
								13	Cyclohexanone	14.5
GWR80	Mesityl oxide	Neat	400	30	NaOH	20.0	100°	18	Acetone	5.2
GWR82	Mesityl oxide	Neat	400	15	NaOH	20.0	100°	18	Acetone	6.8
GWR84	Mesityl oxide	Neat	400	60	NaOH	40.0	110°	18	Acetone	3.9
GWR86	Mesityl oxide	Neat	400	60	NaOH	80.0	110°	18	Acetone	7.7
GWR88(5)	Mesityl oxide	Neat	400	60	NaOH	20.0	110°	18	Acetone	7.0
									Heptane	7.3
GWR44	Acrylonitrile	500 ml. Acetonitrile	33.2	60	--	--	82°	20	Acetonitrile	0.0
GWR48	Acrylonitrile	1000 ml. Acetonitrile	70.4	120	NaOH	3.5	82°	0	Acetonitrile	4.0
								4		5.9
								8		6.4
								12		6.6
								16		6.9
								20		7.1
								24		7.5
									DMF	2.6
GWR74	Acrylonitrile	500 ml. Acetonitrile	31.8	46(6)	NaOH	1.6	82°	24	Acetonitrile	4.6
									DMF	1.7
									DMF(7)	1.2

1. Wt. in grams
2. °C.
3. Time in hours
4. % Organic material ±0.3%
5. Inverse addition of catalyst to reactants
6. Asbestos pre-fired at 1000°C.
7. Boiled in DMF.

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