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NEW ENTERPRISES

CHEMICAL REACTIONS OF ASBESTOS

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SUMMARY Chrysotile asbestos, which has the formula $Mg_6(OH)_8Si_4O_{10}$, has been described as a crystalline hydroxymagnesium silicate polymer; it may be looked upon as mechanically bonded layers or sheets of silicon-oxygen tetrahedra chemically condensed onto magnesium hydroxide layers. The greater bond length of the brucite layers, $(Mg(OH)_2)$ on the outside result in a curvature of the layers to form a spiral "wrapping" or fiber. The gross chemical properties are determined by these surface brucite layers.

The purpose of this report is to define the possible chemical reactions of asbestos and to qualitatively summarize the results obtained with broad classes of reactants; for example, the basic property of chrysotile can be utilized by reaction with acidic organic compounds and by chemisorption. Other reactions of potential utility are base catalyzed ring openings and the addition of asbestos to multiple bond systems.

All the above reactions should be suitable for modification of asbestos fiber surfaces resulting in fibers with different properties such as acid resistance, lubricity, organophillicity, and better cohesion. Asbestos can be looked upon as a cross-linking agent if it is incorporated as a coreactant in the formation of a high organic polymer.

Work completed indicates that carboxylic acids containing other functional groups can be employed to provide an organic surface on asbestos suitable for further reaction. Polymers containing Lewis acid functional groups are strongly adsorbed on asbestos. Future work will exploit these reactions to produce new and potentially useful materials.

INTRODUCTION In 1963 over 700,000 tons of short fiber chrysotile asbestos was consumed in the United States in applications like plastics reinforcement and filler, floor tile, paper treatment, asphalt shingles, molded brake linings, and masonery products such as asbestos cement and acoustical tile.

Research and Development Department
Chemicals Division
Union Carbide Corporation

Union Carbide Nuclear Division has a new wet refining process capable of producing high purity dispersed asbestos at a price of $80-120/ton or conventional short fiber grades of asbestos at $50-60/ton. The Nuclear Division has at least a 100 year reserve of short fiber chrysotile asbestos. However, most short fiber asbestos markets like those listed above are captive markets in established product lines and either new uses for asbestos or improved products employing large quantities of asbestos are necessary to provide a proprietary position for Union Carbide.

The object of the Chemicals Division program is to investigate and establish the chemical reactions of asbestos and to determine whether derived products of asbestos are worthy of specific end-use applications. The quality of products en- corporating asbestos is highly dependent on fabrication techniques; hence a considerable research outlay is required to merely enter existing markets. For this reason conventional applications are not being emphasized until truly promising new products are developed.

Chrysotile asbestos has the general formula $Mg_6(OH)_8Si_4O_{10}$. The structure has been described as a crystalline hydroxymagnesium silicate polymer and is now looked upon as simply layers or sheets of silicon-oxygen tetrahedra chemically condensed onto magnesium hydroxide layers(1) with mechanically interlocking between successive layers. The greater bond lengths of the brucite layers, $(Mg(OH)_2)$, on the outside, result in a curvature of the layers to form a spiral "wrapping" or fiber. Gross chemical properties are determined by the brucite layers on the surface with asbestos ordinarily having chemical properties similar to magnesium hydroxide. Neutralization of the magnesium hydroxide with strong acid solubilizes the magnesium leaving a fibrous silica structure behind. If it is assumed that each magnesium atom in a recurring unit of $Mg_6(OH)_8Si_4O_{10}$ is bound to the silica layer, a total of six -MgOH groups are present for reaction. The other two hydroxyl groups then represent one molecule of water hydrating the silica as two -SiOH groups. It is more likely that the two hydroxyl groups are paired with two magnesium ions existing as adsorbed magnesium hydroxide(2).

Since a structural chrysotile fiber contains 6-10 layers of brucite and silica, the availability of all the OH groups for reaction is uncertain. With strong acids magnesium is extracted stoichiometrically leaving fibrous silica. The first molecule of water (2 OH) is lost at temperatures from 130-370°C. Coalinga CMS grade asbestos is a short fiber dispersed chrysotile corresponding to Quebec number 6 and 7 grades and is composed of bundles of individual fibers.

Chemical modification of asbestos can be directed toward three types of products. First, the asbestos itself can be chemically degraded to useful materials such as magnesium salts and silica.

Since chemical properties of asbestos are determined by surface effects, surface modification of the asbestos can result in significant changes in chemical properties.

Finally, since asbestos is a high inorganic polymer, cross-linking of polymer molecules could lead to strong solid products. The ordinary concept of chemical cross-linking may be inadequate in this context because molecular cross-linking of a comparatively large asbestos fiber may mean only surface modification resulting in stronger fiber interaction and better cohesion. The geometry of the fibers is such that a random packing of fibers will leave spaces larger than molecular dimensions. However, chemical reaction of a very high molecular weight organic polymer with asbestos could result in fiber cross-linking. Asbestos then becomes the minor component and might be considered a cross-linking agent for the organic polymer.

DISCUSSION Three general reactions may be envisioned as potential routes to modified asbestos. First, acids, acid-forming compounds, or acid derivatives may react with asbestos to form simple salts. This reaction is known to occur readily and is accompanied by extraction of magnesium as a magnesium salt.

A second potentially useful reaction is the addition of pendant hydroxyl groups to unsaturated or cyclic compounds. Rings like oxiranes which open under basic conditions are likely candidates.

Finally, chemisorption can result in strong adhesion of polar groups to either acidic or basic sites on the asbestos structure.

POTENTIAL REACTIONS AND PRIOR ART

Inorganic Salts of Asbestos

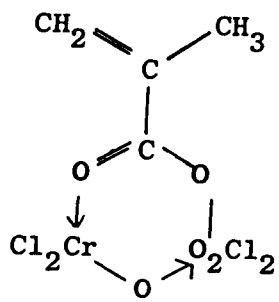
Weak acids will partially add to asbestos by salt formation to modify the asbestos surface or cause cross-linking whereas strong inorganic acids are completely neutralized by asbestos with extraction of magnesium. Patents describe solid products of asbestos bound with fluosilicic acid[4] and alumina sol[5] as well as corrosion resistant coatings from silica sol and asbestos[6]. Asbestos cross-linked with dibasic acids or

polybasic polymeric acids is in reality a high inorganic polymer. Boric acid combines with magnesium carbonate at high temperatures to form a high strength brick[7] and may be a suitable binding or cross-linking agent for asbestos.

Inorganic anhydrides, esters, and acid halides would react with asbestos and produce products similar to those derived from the corresponding acids. The reaction of esters might be useful in lowering magnesium extraction but in aqueous solution, if sufficient reaction time is allowed, hydrolysis of the acid salt would result in equilibrium between the acid and salt as is found on acid addition, and the free acid could extract magnesium. With anhydrides magnesium extraction should parallel that found with acids. Acid halides should cause more extensive magnesium extraction by the hydrogen halide by-product. Alkoxy silanes and halosilanes were reported to provide a reactive asbestos surface by reaction with OH groups[8]. Improved asbestos filled polyethylene can be produced by irradiation of asbestos modified by vinyl silanes[17]. Amino alkyl silanes should be suitable for modifying asbestos prior to cross-linking or condensation polymerization.

$$X_3Si(CH_2)_nNH_2 + YOMgOH \longrightarrow (YoMgO)_3Si(CH_2)_nNH_2$$

A similar surface modifier is methacrylatochromic chloride (I)

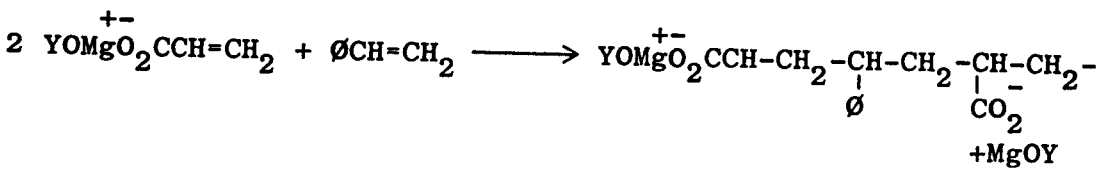


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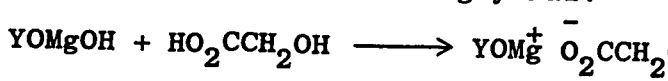
Most inorganic acids and derivatives have ionization constants that are either too large, causing magnesium extraction, or too small, and apparently insufficient for reaction. However, reactivity of very weak acids with asbestos is not clearly defined.

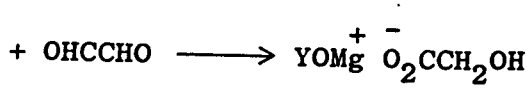
Asbestos Reaction with Organic Acids

Organic acids offer promising candidates for salt formation with asbestos since their ionization constants fall in an intermediate range, making them reactive toward asbestos, but allowing at least some acid addition without total magnesium extraction. Oxalic acid and oxalate salts have been used to treat asbestos paper for high strength properties[11], apparently by cross-linking the fibers. Similar cross-linking should also be observed with polymeric carboxylic acids such as polyacrylic acid. Acrylic acid (or other unsaturated acids) could be applied to asbestos and then copolymerized to provide cross links in a technique like that employed with polyester resins. Thermal



polymerization of the adsorbed acrylate ion could also result in cross-linking. A suitable reactive substrate for condensation polymerization may be achieved by similar reaction of asbestos with glycolic acid or glyoxal:





Various carboxylic acid derivatives or thiocarboxylic acid derivatives may be employed to produce similar products. Carboxylic anhydrides should behave much like the corresponding acid. Ketenes could be expected to add readily at low temperature, perhaps with little magnesium cleavage. Isocyanates also should react. Simple carboxylic esters offer no advantages over acids but lactones, adding as either monomer or polymer would provide a reactive organic hydroxyl group for cross-linking or further polymerization.

Carboxylic acid chlorides have not been studied since evolution of hydrogen chloride can be expected to cause massive leaching of magnesium.

Simple amides and nitriles are relatively stable to hydrolysis and would offer the same problem of slow hydrolysis observed with esters. By-product amines or ammonia could maintain a higher pH so as to minimize magnesium extraction.

Lactams do not undergo ring opening as readily as do lactones but are hydrolyzed much easier than simple amides. Polyvinylpyrrolidone has been used as a binder in strong asbestos paper[14,15] and it is possible that some cross-linking may have occurred by ring opening.

Cyanuric acid has a first ionization constant of 1.8×10^{-7} and should add easily to asbestos with little magnesium extraction. Cross linking might then be effected by partial pyrolysis of the dry, treated asbestos. Any acidic organic material with an ionization constant in the range 10^{-7}-10^{-8} could be a candidate for asbestos treatment.

Other organic acids that might be considered are sulfonic, sulfinic and phosphonic acids. Their high acidities would result in considerable magnesium extraction along with addition. Sultones may add polymerically like caprolactone.

Alcohols and mercaptans are normally very weakly acidic and only highly activated molecules can be expected to add to asbestos. Acetylenes likewise are too weakly acidic to be expected to react. Alkyl halides could react by nucleophillic substitution or by elimination of hydrogen halide. By either reaction the hydrogen halide by-product will extract magnesium.

Addition of Unsaturated Compounds and Cyclic Compounds to Asbestos

The addition of multiply-bonded organic molecules to asbestos would have to take place by addition of hydroxide ion to the multiple bond since magnesium hydroxide is not amphoteric and incapable of yielding a proton even with strong base catalysis. Steric crowding and unfavorable equilibria would certainly make such addition difficult:

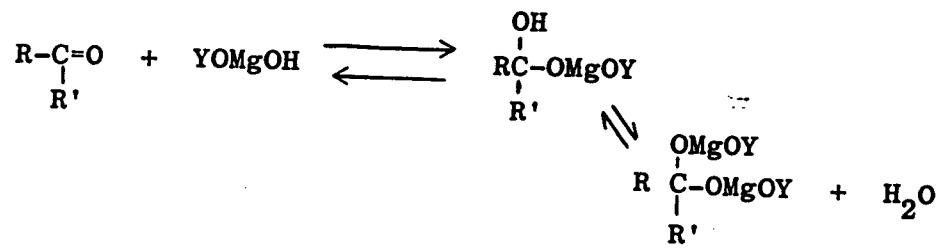
$$YOMg\overset{+-}{O}H + CH_2{=}CHX \longrightarrow HOCH_2\underset{\displaystyle MgOY}{\underset{|}{C}}HX$$

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

Y = asbestos

If -SiOH groups are present on asbestos addition should occur more readily. This problem is further complicated by the tendency of activated vinyl compounds to polymerize. Unactivated vinyl compounds and acetylenes should be unreactive toward hydroxide addition.

The addition of carbonyl compounds may be postulated by the following route:

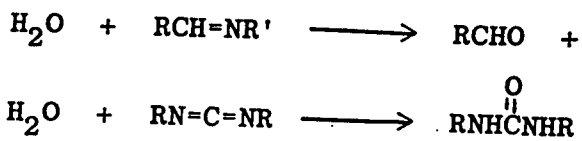


R, R' = alkyl, aryl, H

Y = asbestos

Such reactions are normally acid catalyzed and equilibrium will be far in the direction of the aldehyde or ketone.

Multiply-bonded carbon-nitrogen compounds should resemble carbonyl compounds in reactivity. Schiff bases and carbodiimides are likely to cause asbestos dehydration:



Ring opening of epoxides by asbestos could yield a monomagnesium salt of a glycol or a polyalkylene oxide bonded to asbestos. The treatment of asbestos with a polyamide epoxy resin to produce fiber mats of improved interfiber bonding is described in a patent(16). Epichlorohydrin could be used as a difunctional molecule if magnesium extraction by byproduct hydrogen chloride is permissible.

Thiuranes should undergo ring opening like oxiranes, but alkyleneimines are usually stable to ring opening under basic conditions as are higher cyclic ethers like tetrahydrofuran.

Chemisorption

Asbestos is definitely basic but can have both acidic and basic sites on the polymer spine. Acids should be readily adsorbed on the hydroxyl surface. This is evident in the reaction of carboxylic acids where the rate of adsorption of acid from solution is several times as great as the rate of neutralization of the acid. Polymers containing Lewis acid functional groups

such as ketones, acetals, and nitriles could be adsorbed on the brucite surface of asbestos and behave like graft copolymers of asbestos and organic material. The organic loading on such "grafts" could be controlled by selective extraction of lower molecular weight material through solvent choice. Both addition and condensation polymers could be added to asbestos this way.

Chemisorption could take place at acid sites on asbestos as well as on the brucite surface. However, such sites are much less numerous and chemisorption of bases is likely to be quite weak. If very high molecular weight bases were employed, a noticeable adsorption might be observed.

UNION CARBIDE CHEMICALS DIVISION PROGRAM

The Chemicals Division became actively engaged in asbestos research in 1963 when P. L. Smith and L. C. Shriver began studying the effects of acid on asbestos.

The work thus far has largely ignored product application or evaluation of potentially useful materials and reactions of "unmasked" asbestos, ie, the silica residue after acid extraction of magnesium. This approach will be continued but any reactions that promise ultimate utility and good economics will be thoroughly investigated and the products will be evaluated as commercial materials.

Smith and Shriver found that acid addition to asbestos is in competition with magnesium extraction and that dibasic acids react by both mechanisms to "cross link" asbestos in a solid inorganic product. For example, phosphoric acid (and presumably other strong acids with similar first and second ionization constants) reacts first with asbestos to extract magnesium ion and the magnesium dihydrogen phosphate then acts as a difunctional acid which adds to the asbestos surface[3].

Smith and Shriver also studied maleic and acetic acid[10] and found that magnesium extraction occurs simultaneously with acid addition in the acetic acid reaction. Maleic acid acts as a strong acid to extract magnesium to form magnesium hydrogen maleate which then reacts further by addition to asbestos. Direct addition of magnesium dihydrogen phosphate or magnesium hydrogen maleate solutions to asbestos can also be used to form solid rock-like products. If the strength properties of these products is due to increased cohesion through surface effects, boric acid could prove to be a better and more economical binder than either phosphoric acid or maleic acid.

The addition of acids to asbestos seems to depend on acid strength or pH with carboxylic acids falling into an acidity range capable of both acid addition and magnesium extraction. Polymeric carboxylic acids should be better cross-linking agents than dibasic acids like maleic acid because extracted magnesium can cross-link the organic reagent and a larger molecule is better suited to bridge the large distance between two asbestos fibers. The Plastics Division has reported some success in "cross-linking" asbestos by milling it with an ethylene-acrylic acid copolymer[12]. Aqueous polyacrylic acid is slow to add to asbestos, probably because of molecular bulk and slow diffusion. . Current work indicates that a high loading of acrylic acid can be made on asbestos. The product is hydrolytically unstable but might be incorporated in a vinyl resin. This work is being continued to elucidate the structure of the reaction product, to develope an efficient process, and to investigate the utility of the product as a comonomer in vinyl resins and vinyl cured polyesters.

Unsaturated fatty acids should also be investigated. Asbestos with an unsaturated fatty salt surface might be an excellent thixotropic agent and coating filler capable of vinyl cross-linking reactions.

A few acid derivatives have been examined for reactivity with asbestos. Maleic anhydride, as expected, acts much like maleic acid[3], ultimately forming a hard, cross-linked resin. Toluene diisocyanate reportedly cross links asbestos[13] but in repeating the work, Shriver found that only the surface of the solid product had reacted completely, quite likely by hydrolytic polymerization of the isocyanate to a polyurea[3]. Isocyanate-capped polyether prepolymers also seem to react with asbestos but the evidence is inconclusive. Asbestos does catalyze the dimerization of phenyl isocyanate. A study of catalyzed reactions between asbestos and isocyanates could perhaps be justified, but the chances of successful reaction are poor.

Carboxylic esters are very slow to hydrolyze and quite ineffective in adding carboxylate ion to asbestos. Shriver found little acetate addition on heating aqueous solutions of ethyl acetate or 2-ethylhexyl acetate with asbestos. Heating of dry carbitol acetate with asbestos at 180° for 12 hours gave less than two percent addition of organic material. Ester hydrolysis must be fast to offer any advantages over acid addition since after sufficient time, hydrolysis of the salt results in the same equilibrium whether acid or ester is the starting material and magnesium extraction can still occur.

It is possible that activated esters may be sufficiently more reactive than acetates to allow rapid hydrolytic addition of carboxylate ion. Dialkyl maleates should be investigated because only one ester group is highly activated and could provide a handle for attachment of a vinyl surface to asbestos.

Lactone rings are easily opened in basic solution. Caprolactone added readily to asbestos as polycaprolactone in both aqueous and organic solvents. Magnesium extraction is low, but the rate of caprolactone polymerization was several times faster than the rate of addition to asbestos on a weight basis and organic loading was only 4-8% by weight. The products were hydrolytically unstable. Higher organic loading of asbestos may be possible and the caprolactone polymer byproduct may also add. Other lactones including sultones must be investigated.

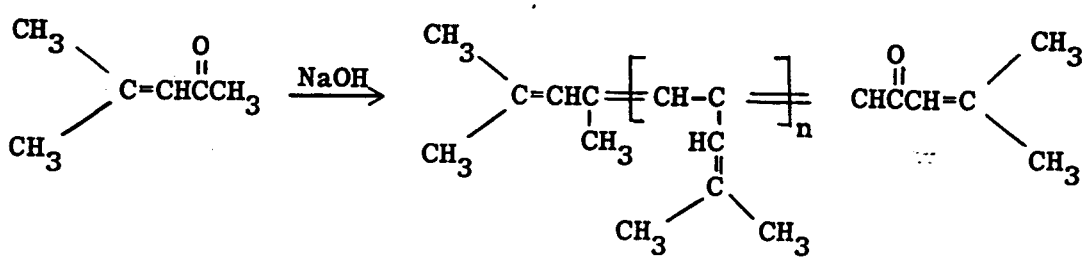
To complete the work on lactones, lactams should also be added to asbestos. Caprolactam does not add under conditions similar to those employed with caprolactone, but the use of a strong base catalyst could result in addition of polymerized material.

Phenol is apparently too weak an acid to react with asbestos. Heating of aqueous phenol with asbestos to 105° and anhydrous phenol with asbestos to 220° lead to no product. It is very likely that strongly activated phenols will react with asbestos. The necessary acidity can be determined by attempting the reaction with various phenols of known ionization constant.

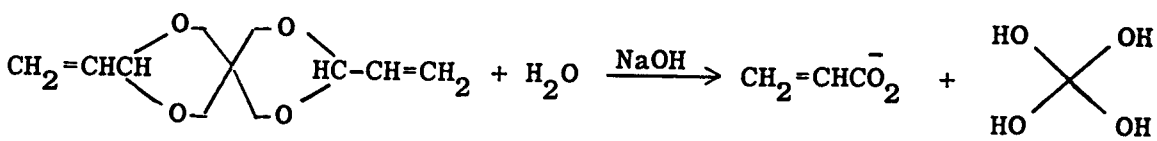
The ionization constant of cyanuric acid makes it ideal as an asbestos modifier. "Asbestos cyanurate" could act as a thermosetting molding powder.

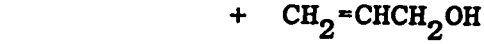
It is unlikely that alcohols can be added to asbestos. 2,6,8-Trimethyl-4-nonanol undergoes dehydration exclusively on being heated with asbestos at 200°.

Attempts to add multiple bonded organic molecules to asbestos have met failure. The addition of asbestos to the double bonds of acrylonitrile, divinyl spirobi-(m-dioxane), and mesityl oxide was attempted in inert solvents. Without catalyst no reaction ensued. In a fashion analogous to conventional cyanoethylation procedures, a solution of acrylonitrile was heated with asbestos and a catalytic amount of powdered sodium hydroxide. The product was asbestos containing 7.5% by weight of polyacrylonitrile strongly adsorbed on the surface. The same procedure was then attempted with mesityl oxide, resulting in a higher aldol condensation product adsorbed on asbestos.



Divinyl spirobi-(m-dioxane) also added to asbestos under sodium hydroxide catalysis, yielding an asbestos acrylate salt containing 8.6% organic material. A disproportionation can be envisioned:





The use of activated vinyl compounds such as divinyl sulfone that are unreactive toward bases is necessary to conclusively determine whether addition of asbestos to carbon-carbon double bonds can take place.

Asbestos modified by polyacrylonitrile, mesityl oxide aldol condensate, or polycaprolactone could not be successfully compression molded. The poor adhesion of the moldings could be due to insufficient organic material or to cross-linking of the organic resin before molding.

One non-acid ring opening was investigated in this program by L. C. Shriver. When propylene oxide is heated with asbestos under high pressure, the starting material is polymerized and apparently some of the polyether is bound to the asbestos either as a magnesium alkoxide or through chemisorption. Such polyether grafted asbestos might be useful as a compatible filler. However, evidence of actual formation of the modified asbestos is inadequate and the product will not be hydrolytically stable.

Chemisorption of acidic species occurs on asbestos as expected. Polyacrylonitrile is strongly adsorbed on asbestos when formed in situ. Polyaldol condensation of mesityl oxide or acetaldehyde on asbestos results in a product that also appears to be due to chemisorption. Other suitable polymers might be formed in situ on asbestos by initiation of vinyl polymerization with ionizing radiation or adsorbed initiator.

The chemisorption of basic compounds by asbestos is questionable. We have found that pyridine when refluxed with dry asbestos and extracted with anhydrous ether, does not adhere to asbestos. A high molecular weight polyamine or polyether might be chemisorbed and would be easily detectable but the value of examining such systems is debatable.

UNION CARBIDE PATENT POSITION

Few patents have been issued on the chemical modification of asbestos. In general, the various patented compositions of matter containing asbestos describe the use of binders and adhesive matrices to produce cohesive products.

Specific patents covering possible reaction products of asbestos include compositions of asbestos and hydrous metal oxides[5], silica sol[6], and fluosilicic acid[4]. Silane modified asbestos is well known and it is likely that only process patents and specific compositions patents for resins filled with silane-modified asbestos are attainable. Such a patent has been issued for the treatment of polyethylene and vinyl triethoxy silane-modified silica with ionizing radiation[19].

Composition of matter patents on carboxylate-modified asbestos include a patent on fibrous sheets from asbestos treated with oxalic acid[11] or a polymer containing carboxyl and carboxamide groups[20]. The use of polyvinyl pyrrolidone[14,15] and an epoxy-polyamide thermosetting resin[16] in high strength asbestos mats and papers have been patented. The addition of metal soaps to disperse asbestos[5,21,22] by formation of a protective colloid is a form of chemisorption.

It appears that any specific new compositions of matter based on asbestos modified by acids or by chemisorption of polymeric materials can be considered patentable. The broad classes of carboxylate or chemisorption-modified asbestos are partly disclosed, limiting patent claims. For example, compositions of asbestos modified by polymerized lactones might be patented as a class. Another patent might cover asbestos modified by unsaturated carboxylic acids. The processes for the production of these materials are also patentable.

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