

THE SURFACE REACTIVITY OF VERMICULITE TOWARDS HEXAMETHYLENE DIISOCYANATE (HMDI)

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Abstract—The reaction of hexamethylene diisocyanate with the surface of heat-activated vermiculite parallels the reactions with the oxides SiO₂, Al₂O₃, MgO considered individually, which a number of authors have already described. The fixation ratio is about 5 molecules per 100 Å² area. Nearly one half of the grafted molecules retain a “free” isocyanate function, which is requisite for a subsequent polyaddition of the processed mineral. The interaction with vermiculite occurs according to three principal processes; (i) formation of a surface urethane, (ii) formation of a surface carbamate, (iii) fixation by hydrogen bonds.

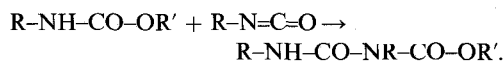
INTRODUCTION

In order to graft urethane functions onto a vermiculite surface and to create a coupling agent between the mineral and a polyurethane foam, we brought hexamethylene diisocyanate (HMDI) into contact with a phyllite powder. The experiments were carried out in such a way that one of the isocyanate functions of the HMDI molecule should remain “free”, with the aim of reacting it subsequently with a polyol (Saunders and Frisch, 1962). A polyurethane matrix, thermally and mechanically reinforced by vermiculite, is thus obtained.

It is well-known that compounds with an isocyanate function can react with materials having an active hydrogen, such as alcohols, to generate urethanes (Normant, 1968; Sykes, 1969):



Moreover, the remaining active hydrogen may bring about a further condensation according to the reaction:



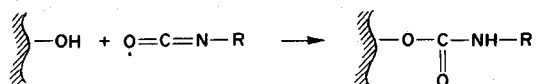
Generally, the reactivity of isocyanates is influenced by steric hindrance and the acidity of the reaction medium. It is higher towards an aliphatic alcohol function than towards a phenolic function, which is more basic.

We have investigated whether, under certain conditions, the hydrogen of the surface hydroxylic functions lining the surface of the phyllite crystals can react in a similar way with isocyanates. Both the Brönsted and the Lewis surface acidity of a phyllite can be increased by a proper dehydration of the silicate. Yet, in the case of vermiculite, the problem is more intricate because of the simultaneous presence in the structure of Si, Mg, Fe and Al. By way of

example, a Lewis acidity is observed with aluminium, but on the contrary with silicon, several bond types may be formed (Forni, 1973; Guillet, 1973; Basila, 1961).

According to Eley *et al.* (1973), isolated MgOH type hydroxylic groups react in the same way as silica hydroxyls to produce urethanes. In any case, with Al as well as with Si and Mg, as soon as the hydroxylic groups are closely packed enough as in the case of molecular water, the reaction with isocyanate occurs with urea formation (Cram and Hammond, 1964).

The reaction visualizing the formation of an urethane bridge would be as follows:



This reaction has been observed and studied in the case of “Aerosil” silicas and aluminas with high surface areas (200 m²/g) and with compounds such as methyl isocyanate (Guillet, 1973), ethyl isocyanate (Eley *et al.*, 1973; Lange, 1968; Weldes, 1965) and butyl isocyanate (Kulik *et al.*, 1970; Guillet, 1973). According to these studies, the nature of the products formed depends on the adsorption temperature of the isocyanate and on the temperature at which the oxide surface has previously been evacuated. The activity and the surface acidity are related directly to the dehydration temperature which governs the formation and the content of “isolated” surface hydroxylic groups. However, in the case of swelling clay minerals, such as vermiculite, supplementary difficulties are encountered.

The dehydration under vacuum of a phyllite leads to the elimination of both the molecular and the hydration water of the interlayer cations. There is a risk, too, of impairing the structure by removing constitutional hydroxyls and this especially may take place when the dehydration occurs under vacuum. Con-

versely, if the mineral has not been properly dehydrated, the presence of water will cause hydrolysis of the isocyanate with urea formation (Cram and Hammond, 1964), and possibly a polycondensation of the organic compound (Shaskova *et al.*, 1960).

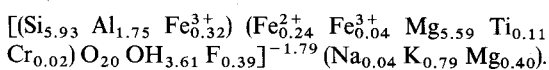
The factors which play a part in the phenomenon of interaction and isocyanate grafting on the vermiculite are thus, essentially (i) the vacuum dehydration temperature which settles the acidity level and the content of surface "isolated" hydroxyls of the mineral, (ii) the temperature at which the isocyanate reacts with the "activated" mineral, (iii) a third factor arises: the process used to bring the organic compound and the mineral into contact. When powdered vermiculite is used, it is recommended to use a solvent in order to preclude the polycondensation reactions of the diisocyanate.

MATERIALS

We have used a natural phyllic silicate sold under the name of "crude vermiculite" by the company "La Vermiculite et la Perlite", which originates from the Palabora mines in Transvaal (South Africa). We used it as a powder having the following granulometric distribution:

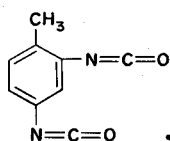
$\phi > 0.250$ mm	1.6%
$0.250 < \phi < 0.125$ mm	12.0%
$0.125 < \phi < 0.100$ mm	10.2%
$0.100 < \phi < 0.050$ mm	59.0%
$\phi < 0.050$ mm	17.2%

Le Dred (1968), Wey and Le Dred (1964) obtained the following chemical formula for this mineral.



The mineral is a trioctahedral vermiculite intermediate between a mica (biotite) and a vermiculite. It is composed of sequences of mica layers, sequences of vermiculite layers and a seemingly regular interstratification between these two kinds of layers. However, the mica content is low compared to the vermiculite, or the interstratified mica-vermiculite mineral content. Some authors call such a mineral hydrobiotite. The powdered vermiculite which we used exhibits a $16.5 \text{ m}^2/\text{g}$ surface area, measured with argon according to the BET method.

"Fluka" pure hexamethylene-diisocyanate (HMDI) was used corresponding to the formula $\text{O}=\text{C}=\text{N}-(\text{CH}_2)_6-\text{N}=\text{C}=\text{O}$. It is a syrupy, colorless liquid with a density of 1.05, a boiling point of 83°C , and is comparatively soluble in aromatic solvents. Several orientation tests were carried out on an aromatic diisocyanate, the 2-4 toluene diisocyanate:



METHODS

The number of bound diisocyanate molecules is measured through the determination of the total nitrogen content by the Kjeldahl micromethod. The substances are mineralized in concentrated sulfuric acid in the presence of a catalyst (Se, K_2SO_4 , CuSO_4), with heating. The ammonia is next removed in an alkaline medium, carried over with steam and complexed by a 3% solution of boric acid. Afterwards it is titrated with a solution of hydrochloric acid.

To accomplish the reaction of diisocyanate with powdered vermiculite three different processes were tried.

Reaction in vapor phase

The HMDI grafting in the vapor phase has the advantage of using only a small amount of substance and the possibility of recovering the powder without any washing. By means of the device shown in Figure 1, the vermiculite was dehydrated for 15 hr under a vacuum of 10^{-2} Torr at a temperature between 300 and 500°C .

After cooling the vermiculite and the diisocyanate saturated vapor were brought into contact at a temperature (T) (reaction temperature). The reaction was carried out by putting the whole apparatus (stopcock B closed and stopcock A open) into an enclosure at a temperature (T), which dictates the pressure of the saturated vapor. After contact, the physisorbed diisocyanate is removed by evacuation (A closed, B open) and trapped with liquid nitrogen.

This device does not allow a satisfactory diffusion of the diisocyanate vapor into the powder. Only the top reacts fully with the reagent. The fixation ratios thus may be considered as obtained by default. Table 1 exhibits the values from two experiments carried out with HMDI, which are compared to two further ones, performed with toluene diisocyanate. The amount of bound diisocyanate was estimated through the determination of the whole nitrogen content, according to the Kjeldahl method. The diisocyanate fixation is poor. In the most favorable case the amount fixed by the mineral is 0.62 molecule/ 100\AA^2 area. The highest temperature at which this experiment was performed was 190°C .

Reaction in the liquid phase

To improve the grafting ratio, the previously dehydrated vermiculite was brought into contact with

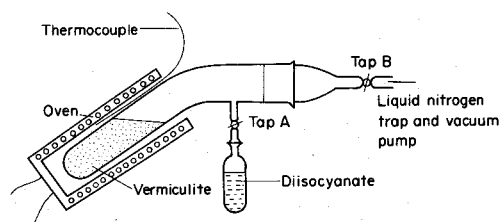


Figure 1. Experimental apparatus for reacting HMDI vapor with vermiculite.

Table 1. Reaction of hexamethylene diisocyanate in the vapor form with vermiculite

Conditions	Hexamethylene diisocyanate		2-4 toluene diisocyanate	
	1	2	3	4
Dehydration temperature under 10^{-2} Torr (duration: 15 hr)	480°C	450°C	400°C	450°C
Reaction temperature (duration: 5 hr)	190°C	160°C	175°C	175°C
Evacuation (duration: 2 hr)	160°C	160°C	160°C	160°C
Number of mole $\times g^{-1}$ of vermiculite	1.7×10^{-5}	1.2×10^{-6}	6×10^{-6}	3×10^{-6}
Number of bound molecules per 100 \AA^2 area	0.62	0.043	0.21	0.109

the liquid diisocyanate. The mineral was heated between 300 and 380°C under a vacuum of 10^{-2} Torr, in the apparatus shown in Figure 2. After cooling, HMDI was poured onto the powder and the enclosure heated at 230°C. After completion of the reaction, the excess diisocyanate was removed by evacuation at 200°C.

The results of these experiments are represented in Table 2. In experiments 2 and 3, a crust appears at

the top of the mineral. At the bottom of the sample, a comparatively large amount of diisocyanate was bound on the mineral. The excessively large number of molecules fixed per 100 \AA^2 indicates a copolymerization of the organic substance. The amount of diisocyanate bound on the mineral through this method exceeds the limit of the formation of a monolayer. In this kind of process the paramount problem is the homogenization of the reaction medium. The problem is magnified by using a powdered vermiculite and by the high viscosity of the diisocyanate.

Reaction in solvent medium

An experiment was carried out in a solvent medium, using the same apparatus (Figure 2) in order to avoid the drawbacks of the previous process. This method uses much less diisocyanate but a low volatile aprotic solvent was required. We used toluene (boiling point 110°C). A mixture with the volumetric proportions 1/20 of diisocyanate in toluene was poured, under vacuum and at room temperature, on a vermiculite which was previously dehydrated at 350°C under 10^{-2} Torr. The system vermiculite-diisocyanate was next heated under reflux at about 110°C for 8 hr. The vermiculite was oven-dried at 160°C after washing and rinsing with toluene and benzene.

Under these conditions a fixation of 6×10^{-5} mole of diisocyanate per gram of vermiculite has been

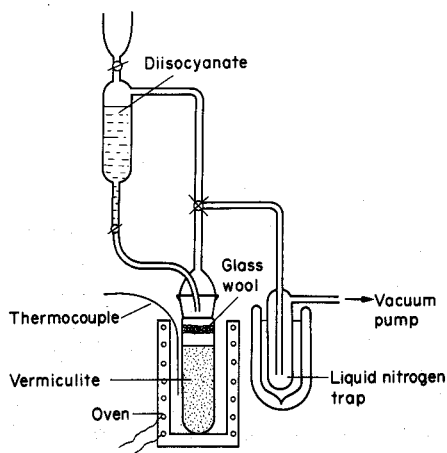


Figure 2. Experimental apparatus for reacting liquid or dissolved HMDI with vermiculite.

Table 2. Reaction of hexamethylene diisocyanate in the liquid form with vermiculite —Reaction temperature 230°C (8 hr) —Evacuation temperature 200°C (15 hr)

	1	2	3
Dehydration temperature under 10^{-2} mm Torr (15 hr)	320°C	350°C	380°C
Number of mole $\times g^{-1}$ of vermiculite	3.46×10^{-4}	4.35×10^{-4} (bottom) 24.8×10^{-4} (top)	1.4×10^{-4} (bottom) 2.8×10^{-4} (top)
Number of bound molecules per 100 \AA^2 area	12.63	15.87 (bottom) 90.52 (top)	5.11 (bottom) 10.22 (top)

observed, which corresponds to a grafting ratio of 0.36 molecule/100 Å² area. A 100 Å² surface fragment of a vermiculite layer may contain a maximum of 16 oxygen atoms. In the most favorable case only 16 surface hydroxylic groups may be present per 100 Å² (taking the diameter of an oxygen atom in the tetrahedral layer to be 2.50 Å).

Assuming that each "isolated" hydroxyl may react with one molecule of diisocyanate and not taking into account steric hindrance and a possible polymerization, the theoretical and maximum amount of bound diisocyanate would be 4.38×10^{-4} mole/g of vermiculite. This value corresponds to a monolayer of organic compound. As all hydroxyls are closely situated, only a low ratio of urethane bridgings may arise under such conditions and the formation of urea or of polycondensation products is much more likely. We tried therefore to determine the "isolated" surface hydroxyls, which alone may react with the isocyanate and yield stable bonds.

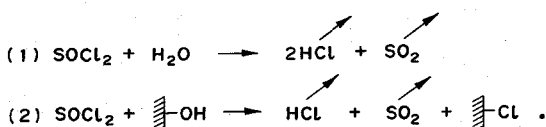
RELATIONSHIP BETWEEN "ISOLATED" SURFACE HYDROXYLS AND THE GRAFTING RATIO

We endeavored to set up a relationship between the content of "isolated" surface hydroxyls of the vermiculite layers and the reactivity of the isocyanate functions. Our aim was to find the limiting conditions of monolayer diisocyanate grafting, without formation of urea or polycondensation products.

Determining the content of "isolated" surface hydroxyls of vermiculite

Among the various methods proposed to determine the hydroxylic groups at the surface of mineral oxides (Donnet, 1969; Boehm and Schneider, 1959, 1962; Fripiat *et al.*, 1962; Basila, 1962; Imelik *et al.*, 1963; Peri, 1965), we selected the hydrolysis reaction of thionyl chloride (Boehm, Schneider and Arendt, 1963). Thionyl chloride reacts with molecular water or with "closely situated" hydroxyls (possibly linked by hydrogen bridgings) to yield hydrogen chloride which is carried away by evacuation. Conversely, an "isolated" hydroxyl will be substituted by a chlorine atom, firmly bonded to the surface. We assume this simple reaction to be specific enough for the surface and "isolated" hydroxyl groups:

In this way:



According to Folman and Yates (1958), sulphurous anhydride does not become fixed on the hydroxylic groups so that the active sites are not blocked in proportion as the reaction proceeds. On the other hand the presence of SO₂ does not prevent the determination of chlorine ions recovered by stirring the mineral

in water, hydrochloric acid being previously carried away by evacuation with heating. Guillet (1973) showed that, in the case of alumina, thionyl chloride reacts essentially with "isolated" hydroxyls.

Our investigations were carried out using a powdered vermiculite dehydrated under vacuum ($<10^{-4}$ Torr) at temperature between 300° and 400°C for 24 hr (Figure 3). After cooling, the powder was brought into contact with thionyl chloride vapor at room temperature for 24 hr and then evacuated at 150°C for at least 12 hr. After evacuation a part of the powder was taken up with a known volume of water and stirred for several hours. The chloride ions were determined potentiometrically.

The results are collected in Table 3 and shown in Figure 4. The substitution of "isolated" hydroxylic groups by chlorine atoms rises to a maximum at 370°C, the dehydration temperature of vermiculite. This temperature corresponds, for the mineral surface to the presence of a maximum number of "isolated" hydroxyls (6.2 OH/100 Å²).

The ratio decreases sharply above 370°C. We may assume that the "isolated" hydroxyl groups begin to be eliminated and siloxane bridges come into being on the mineral surface. On the other hand, the temperature should not be too high so as to retain the vermiculite structure. Owing to this sharp decrease of the "isolated" hydroxyl content, we may suspect that the structural hydroxyls begin to get away. This value (6.2 OH/100 Å²) seems thus to be excessive and considered as a limiting value. However, at 310°C the hydroxyl content amounts barely to 3.9 OH/100 Å². This value approximates those recorded by some authors for silica gels (Peri and Hensley, 1968). The limiting value of 6.2 OH/100 Å² area allows the calculation of the limiting amount of diisocyanate actually fixed through chemical bonding.

Assuming that each "isolated" hydroxyl reacts with one of the functions of the organic molecule, disregarding steric hindrance and a possible polymerization, we obtain the maximum value of fixation at 370°C: 1.7×10^{-4} mole/g of vermiculite. This value corresponds to a diisocyanate monolayer lining. Any values exceeding this datum will point to an overstepping of the grafting ratio, i.e. a loss of organic compound through hydrolysis or polycondensation.

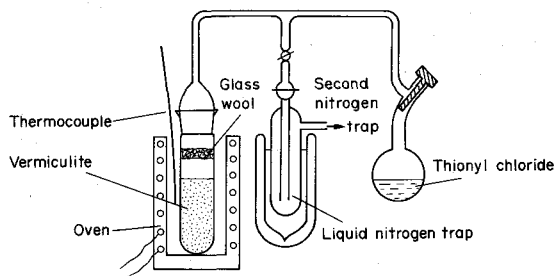


Figure 3. Apparatus for thionyl chloride adsorption onto vermiculite.

Table 3. Number of gram-equivalents of "isolated" hydroxyls per gram of powder

Dehydration temperature under 10^{-4} Torr	Number of g-equivalents of "isolated" OH/gram of powder
310°	1.08×10^{-4}
330°	1.19×10^{-4}
350°	1.28×10^{-4}
370°	1.70×10^{-4}
380°	1.52×10^{-4}
405°	0.90×10^{-4}

INVESTIGATION OF HEXAMETHYLENE DIISOCYANATE GRAFTING ON VERMICULITE

We noticed that the content of "isolated" surface hydroxyls in vermiculite rises to a maximum at 370°C. Our first survey consisted of checking that the maximum diisocyanate lies at this very temperature. With this aim, we turned to the process of contacting in a solvent medium which proved most easy to put into practice and which yielded results approximating most closely the limiting grafting ratio (1.7×10^{-4} mole/g).

Influence of the dehydration temperature of the mineral

Owing to the aforementioned grounds, the dehydration temperature parameter governs the reactivity of the mineral towards the diisocyanate. The grafting experiments were carried out under the following experimental conditions. A mixture 1/10 parts by volume of HMDI in toluene was prepared. The vermiculite previously dehydrated at a temperature (T) under a 10^{-2} Torr vacuum was brought into contact with the diisocyanate solution, out of contact with air. The whole solution + powder was heated with refluxing under atmospheric pressure at 110°C for 8 hr. The powder was rinsed several times with toluene and benzene and dried at 130°C.

The ratio of bound HMDI on the powdered vermiculite was estimated by determination of the whole nitrogen content through the Kjeldahl micromethod. The number of isocyanate functions left "free", i.e.

unaffected is evaluated by a colorimetric method which can be summarized as follows: excess butylamine is added to the isocyanate. The reaction with butylamine yields an urethane: $R-NCO + R'-NH_2 \rightarrow RNH-CO-NHR'$. The excess butylamine reacts next with the oxalate of malachite green and a colorless compound is formed (Kubitz, 1957).

About 1 g treated vermiculite was shaken in a tetrahydrofurane *n*-butylamine solution (10 ml) for 2 hr. The solution was reclaimed by filtration. A given volume of this solution was added to an equal volume of pyridine solution of malachite green. This mixture was colorimetrically analyzed at 615 nm. The chief problem was water contamination: the samples must be kept away from water. The carefully dried analyzed standards and samples must have fairly similar weights. A possible adsorption of butylamine between the vermiculite layers also must be taken into account (Siedskind, 1963). This extra amount of consumed butylamine must be subtracted from the overall consumption. This can be achieved by careful standardization.

The results of the analysis are collected in Table 4, and plotted in Figure 5. A maximum isocyanate fixation is actually evidenced, at about 370°C (Curve A). However, the amount of diisocyanate fixed by vermiculite at this temperature exceeds barely half of the limiting ratio, which was previously stated

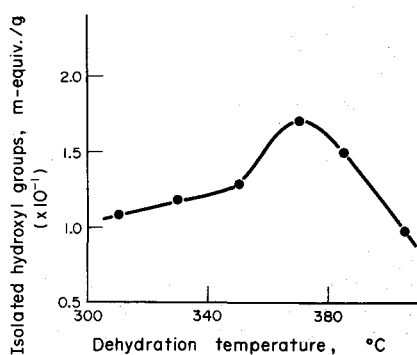


Figure 4. Number of "isolated" hydroxyl groups vs. dehydration temperature.

Table 4. Amount of HMDI fixed on powder and number of "free" isocyanate functions

Dehydration temperature (°C)	300	320	330	350	370	390
Sample number	1	2	3	4	5	6
Number of mole/g of vermiculite	10.2×10^{-5}	6.87×10^{-5}	7.15×10^{-5}	8.7×10^{-5}	9.5×10^{-5}	9.28×10^{-5}
Number of g equivalents of free functions (-N=C=O) per/g of vermiculite	2.5×10^{-5}	1.0×10^{-5}	1.0×10^{-5}	1.25×10^{-5}	1.5×10^{-5}	1.5×10^{-5}
Percentage of "free" functions (-N=C=O) in proportion to bound diisocyanate	24.5%	14.5%	14%	14.4%	15.7%	16%

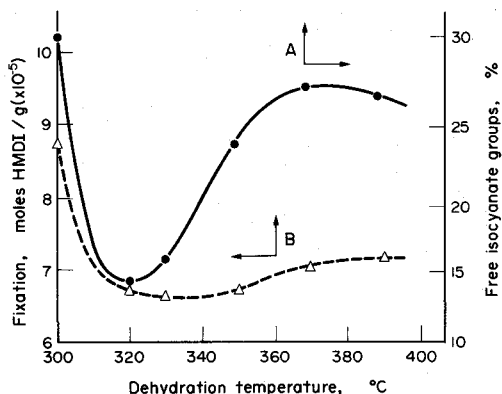


Figure 5. Number of HMDI moles grafted on the powder (A) and percentage of "free" isocyanate groups (B) vs. dehydration temperature.

(0.95×10^{-4} instead of 1.7×10^{-4} mole/g). Moreover, a singular point arises on the curve at a temperature of 300°C . The abnormally high fixation ratio at this comparatively low temperature may, no doubt, be accounted for by the presence of condensed diisocyanate, originating from the hydrolysis of the organic compound on contact with an incompletely dehydrated mineral.

The bottom line of Table 4 displays the percentages of residual unaffected isocyanate functions. The percentages were calculated by assuming that a molecule of mineral-grafted diisocyanate can have only a single "free" isocyanate function, the other one being bonded to a structural hydroxyl. It appears that the percentage of "free" functions is low and constant (about 15%) in the range of temperatures investigated (Figure 5) (Curve B).

The organic molecule would therefore react with almost the whole of both its isocyanate functions. A reaction of both functions with two neighbouring hydroxyls belonging to the phyllic structure may be assumed. Polymerization and polycondensation of the organic molecules to each other also may be considered (Sayigh *et al.*, 1972). It is noteworthy that the 370°C temperature corresponding to the maximum diisocyanate fixation is an intermediate between those which were recorded in the case of amorphous alumina (430°C) and silica (300°C) (Guillet, 1973).

Influence of the reaction temperature

We checked the influence of the heating temperature of the mixture powder + solution, i.e. the reac-

tion temperature between the isocyanate functions and the OH radicals of the mineral. Working under the same conditions as in the case of experiment No. 5 (Table 4), but without heating the (solid + solution) mixture (250°C), the vermiculite fixes only 6.1×10^{-5} mole instead of 9.5×10^{-5} mole/g of solid product. The grafting reaction was enhanced by temperature. However, in our operative conditions, we are restricted to a maximum temperature of 110°C , the boiling point of the solvent.

Influence of the interlayer cations

Replacing the initially calcium and magnesium powdered interstratified mineral by the sodium interstratified mineral (which is obtained after ion exchange) brings about lower fixation ratios under the same operating conditions. The chemical composition of the mineral being the same, the variation of the grafting ratio can be accounted for only by a difference in hydration of the mineral, connected with the interlayer exchangeable cations.

Influence of the concentration HMDI/toluene and of the reaction time

Until now we have been bringing into contact 20 g of vermiculite and a solution of 10 cm^3 HMDI per gram of mineral, which means a large excess in regard to the expected grafting ratio (1.7×10^{-4} mole/g). We endeavored to decrease the HMDI concentration and to increase the reaction time. Twenty grams of mineral heated at 370°C under a 10^{-4} Torr vacuum during 24 hr, are reacted with a HMDI volume between 0.5 and 10 cm^3 , the final volume of the solution being 100 cm^3 . Table 5 and Figure 6 show that the grafting ratio is promoted by reaction time. In the case of experiments 2 and 3, 10% of the HMDI

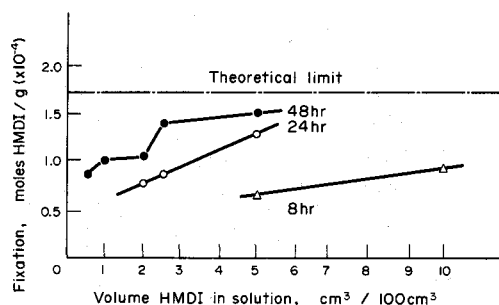


Figure 6. Number of HMDI moles grafted per gram of vermiculite vs. HMDI volume in toluene solution.

Table 5. Number of bound HMDI moles per gram of vermiculite versus the number of starting HMDI cm^3

Reaction time	HMDI volume/100 cm^3 solution (toluene + HMDI)					
	Exper. 1 10 cm^3	Exper. 2 5 cm^3	Exper. 3 2.5 cm^3	Exper. 4 2 cm^3	Exper. 5 1 cm^3	Exper. 6 0.5 cm^3
8 hr	0.95×10^{-4}	0.65×10^{-4}				
24 hr		1.28×10^{-4}	0.84×10^{-4}	0.75×10^{-4}		
48 hr		1.5×10^{-4}	1.42×10^{-4}	1.04×10^{-4}	1.04×10^{-4}	0.82×10^{-4}

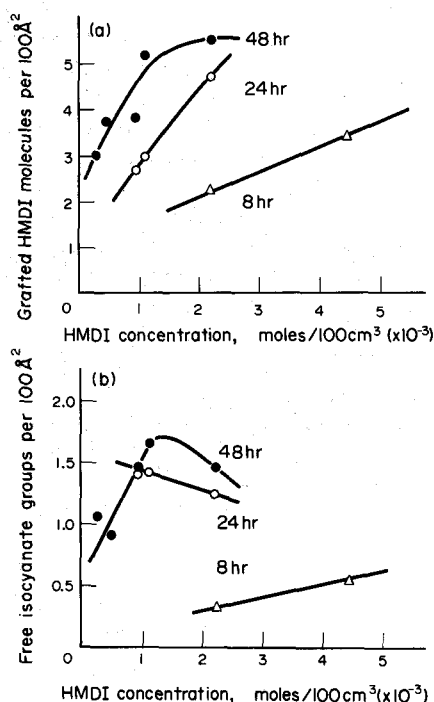


Figure 7. Number of grafted HMDI molecules per 100 Å² (a) and number of "free" isocyanate groups per 100 Å² (b) vs. HMDI volume in toluene solution.

have been fixed after 48 hr and the grafting ratio is about 1.5×10^{-4} bound molecules per gram of vermiculite, a value close to the theoretical limit (1.7×10^{-4} mole/g). This corresponds to a large excess of reagent: 2.5 or 5 cm³ of HMDI/100 cm³ solution, i.e. 1.1 or 2.2×10^{-3} mole/g vermiculite. The previous results were supplemented by a titration of the residual isocyanate functions, to ascertain if these conditions promote the preservation of a maximum amount of "free" isocyanate functions. The results are summarized in Tables 6 and 7. Table 6 shows that the starting HMDI concentration hardly has any influence on the amount of isocyanate groups. The most favorable concentrations are situated between 2 and 5 cm³ of HMDI in 100 cm³ of

solution. If the percentage of "free" functions in regard to bound HMDI is considered, the most satisfactory result was recorded for a concentration of 2 cm³/100 cm³ solution, which corresponds to 0.88×10^{-3} mole of HMDI in solution per gram of vermiculite (Table 7). To sum up, the following conditions lead to the most satisfactory results: a HMDI concentration in the solution of 1 to 2×10^{-3} mole/g of vermiculite and a reaction time of 48 hr.

DISCUSSION OF RESULTS

The results of the previous paragraphs convey a fuller meaning if the variation of the number of grafted molecules per 100 Å² and the number of residual isocyanate functions are plotted versus the starting concentration of HMDI in the solution (Figure 7a and b). The general form of these curves provides evidence that the maximum grafting is achieved with a reaction time of 48 hr and a HMDI concentration of about 2×10^{-3} moles per 100 cm³ of solution. If these conditions are fulfilled, 5.5 molecules/100 Å² area are bonded, a value which is very close to the theoretically calculated limit of 6.2 molecules.

If the HMDI concentration is slightly lower, the number of "free" isocyanate functions rises to a maximum value of 1.7/100 Å² area (Figure 7b). Accordingly, the optimum grafting conditions lie in a concentration of about 1.5×10^{-2} mole of HMDI per liter of toluene solution and a reaction time of 48 hr. Taking into account the steric hindrance of the HMDI molecule, the aforementioned values provide evidence that a monolayer is practically achieved (85%). Moreover, from a theoretical point of view, a ratio of 1.5–2 "free" isocyanate functions per 100 Å² seems correct. As a matter of fact, a copolymerization between "free" functions is bound to occur at a higher ratio.

BONDING BETWEEN THE ORGANIC COMPOUND AND THE MINERAL

We endeavored to define more precisely the interaction between vermiculite and the diisocyanate by X-ray powder diffraction and infrared absorption.

Table 6. Number of gram-equivalents of isocyanate functions per gram of vermiculite

Reaction time	HMDI volume/100 cm ³ solution					
	Exper. 1 10 cm ³	Exper. 2 5 cm ³	Exper. 3 2.5 cm ³	Exper. 4 2 cm ³	Exper. 5 1 cm ³	Exper. 6 0.5 cm ³
3 hr	0.15×10^{-4}	0.10×10^{-4}				
24 hr		0.35×10^{-4}	0.40×10^{-4}	0.40×10^{-4}		
48 hr		0.40×10^{-4}	0.45×10^{-4}	0.40×10^{-4}	0.25×10^{-4}	0.30×10^{-4}

Table 7. Percentage of "free" isocyanate functions

Reaction time	Exper. 1 10 cm ³	Exper. 2 5 cm ³	Exper. 3 2.5 cm ³	Exper. 4 2 cm ³	Exper. 5 1 cm ³	Exper. 6 0.5 cm ³
8 hr	16%	15%				
24 hr		27%	47.5%	53%		
48 hr		27%	32%	38.5%	24%	36.6%

X-ray diffractometry provides hardly any information. It is difficult to check whether the crystallographic parameters of the mineral undergo any modification through a possible introduction of diisocyanate between the layers. In fact, the organic solvent itself modifies the parameters.

It is hard, too, to furnish any precise information through infrared spectrometry about the bondings occurring in the mechanism, because of the low surface area of the mineral, the quick water contamination in the samples, and the low intensity of the absorption bands. These appear merely as a slight superimposition on the vermiculite bands. Figure 8 brings together for comparison the infrared absorption spectra between 4000 and 1400 cm^{-1} of experiment 3 (Table 5—24 hr of reaction) and of untreated vermiculite. It was recorded starting from treated vermiculite on a CaF_2 plate. We did not succeed in making up autorestant thin films of vermiculite. We distinguish three spectral areas.

The area 3200–3800 cm^{-1}

The domain of the valence vibrations of OH and NH_2 groups, provides information about the surface modifications of the mineral. On the spectrum of pure vermiculite, the band is shifted towards lower frequencies, probably due to supplementary hydrogen bonds, either between paired hydroxyl and amino groups, or between a hydroxyl and an amino group.

The area bordering 2250 cm^{-1}

The pseudoasymmetric vibration band $-\text{N}=\text{C}=\text{O}$, specific of isocyanate function, is located in this region. Generally this band is at 2290 cm^{-1} for vapor phase isocyanate and is shifted to 2273 cm^{-1} as an adsorbed phase upon alumina. Our spectrum exhibits a band shift from 2290 cm^{-1} to 2280 cm^{-1} (Volkmann, 1972). The isomeric form $\text{O}=\text{C}=\text{N}$ and the cyanate free ion are excluded since they adsorb around 2220 cm^{-1} . The 2280 cm^{-1} band may be interpreted as a clue pointing to an interaction and a possible bonding between a surface metallic cation and the isocyanate function.

The area stretching above 1800 cm^{-1} and bordering on 1300 cm^{-1}

This region represents the valence vibrations $\text{C}=\text{O}$, $\text{C}=\text{N}$ and COO . It provides information about the

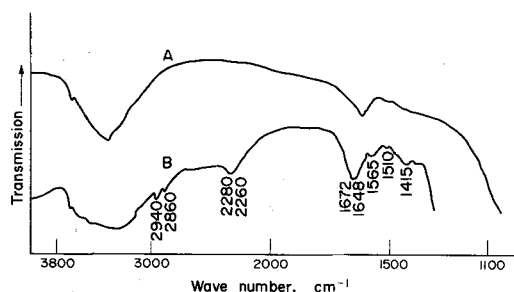
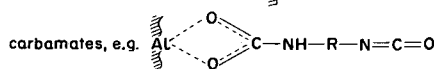


Figure 8. Infrared absorption spectra of (A) vermiculite and (B) HMDI treated vermiculite.

fixation form of the chemisorbed species. In this spectral area, bands are seen at 1672, 1648, 1565, 1510 and 1415 cm^{-1} .

Sokol'skii *et al.* (1971), Eley, Kiwanuka and Rochester (1973) and Volkmann (1972) place the vibration bands of the $-\text{NH}-\text{C}(=\text{O})-\text{O}$ of the aliphatic polyurethanes at 1695 and 1538 cm^{-1} . Moreover, Guillet (1973) and Colthup *et al.* (1964) recorded in the same area bands at 1470, 1590 and 1630 cm^{-1} due to the formation of surface carbamate. In this case it is very difficult to ascribe the bands of our spectrum. We have to assume that various bonds arise simultaneously during the interaction between the isocyanate and the vermiculite surface. Among these, may be mentioned the likely formation of:



and hydrogen bonds with the hydroxyls.

Moreover, the comparatively wide breadth of the vibration bands might be accounted for by the simultaneous formation of bonds with the various oxides (SiO_2 , Al_2O_3 , MgO and Fe_2O_3) which make up the mineral.

CONCLUSION

Hexamethylene diisocyanate reacts with the vermiculite surface, activated in a way similar to that described by some authors for the oxides SiO_2 , Al_2O_3 and MgO , taken separately. Under certain operating conditions, over one third of the bound molecules retain a "free" isocyanate function, which is in a position to initiate a subsequent polymerization of the mineral treated with a polyol.

A grafting ratio of 5.2 diisocyanate molecules/100 \AA^2 area was thus recorded, of which 1.5–2 grafted molecules retain "free" one of their isocyanate functions. The bonds which arise between the surface of the mineral and the organic compound are very likely of the urethane and carbamate type.

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