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WATER PROOFING LINER

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(57) Claim

1. A waterproofing laminate comprising a support sheet united with a waterproofing layer, said waterproofing layer being formed from a plastic mass containing particulate smectite clay mixed with liquid, at least a portion of said liquid being water.

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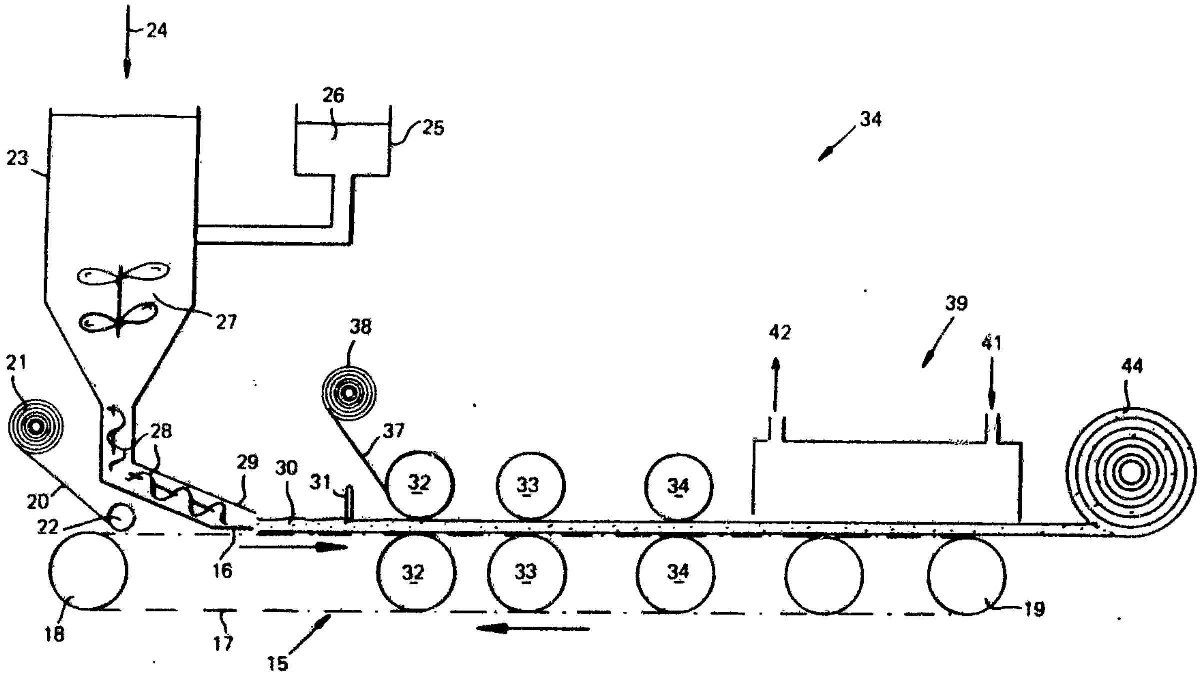

(57) Abstract

There is described a water-proofing material (10) basically made from a plastic mass containing a liquid and particulate smectite clay, usually montmorillonite such as bentonite, which can be united with a carrier sheet (20). The plastic mass can contain aqueous and/or non-aqueous liquid which can be expelled after forming. The smectite clay can be a smectite liner intercalation complex and the mass is desirably formed by extrusion, in the latter case preferably during reaction of the clay and can have a density of at least 1000 kg m^{-3} and can be 1 m or more wide.

WATER PROOFING LINER

This invention relates to a waterproofing material suitable for waterproofing ponds, lakes, lagoons or comparable sites whereby water is retained, or wherein waste is deposited and the ground beneath has to be protected against leakage of aqueous or other liquid. The material can also be used in relation to water proofing structures, covering contaminated land to prevent flow of water into such contaminated land and lining trenches which separate contaminated areas from clear areas. The material can also be used as roofing material on flat or sloping roofs. Several materials have been proposed in the past which include a layer of swellable smectite such as montmorillonite and/or ~~sponite~~ saponite incorporated within the material to act as the sealing agent. The montmorillonite has been carried by a support layer or base which has been provided in various ways. A support layer acts as protection but also gives additional strength within the material.

European patent number 59625 (CLEM) describes a waterproofing material which is a laminate comprising a fabric base, particles of montmorillonite adhered to the base and a scrim adhered over

AUSTRALIAN PATENT OFFICE

the montmorillonite particles to retain them on the base. The CLEM specification requires as an essential feature thereof that the base be capable of venting gas. Although venting of gas from beneath a contained body of water or other matter can be an advantage, it is a great disadvantage to incorporate such ventibility into the actual base. Although there are few sites where venting is necessary it is, when venting is needed, desirable to provide a separate venting layer quite separate from the waterproofing material overlapping the first sheet ~~(10). The~~ In Fig. 1 the sheet (10) has a venting base (13), a layer of montmorillonite (14) adhered to the base (13) and a scrim (15) on top of the montmorillonite. In similar manner sheet (12) has base (16), montmorillonite (17) and scrim (18). As will be seen from the drawing and the arrows (19) the layer of base (16) overlying the montmorillonite (14) provides a path, between the two layers of montmorillonite (14) and (17) which, because it is designed to vent air can also allow liquid such as water to wick out along the path indicated. Thus, the incorporation of a venting base in the sheets (10) and (12) can have undesirable results.

Figure 2 shows how the construction described in European patent application 246 311 (McGROARTY) overcomes these problems. In the MCGROARTY construction a lower sheet (19) has a base (20) and montmorillonite (21). An overlaid sheet (22) has base (23) and montmorillonite (24). In McGROARTY the base (20) and (23) are of solid plastics non-venting and impermeable material. Thus in the construction shown in figure 2 the base (23) forms a non-

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water transmissive layer between the two layers of montmorillonite (21) and (24) thus giving a very good seal. This is a significant advantage over the prior art of figure 1.

Unfortunately, however, the McGROARTY construction does have several practical, other difficulties. Firstly, the bases (20) and (23) are made from a thick, impervious and essentially solid plastics material, described in the specification as HDPE.

Further, the specification describes the fact that granules of montmorillonite are adhered not only to the base but also to each other.

Waterproofing materials of this kind are usually supplied in rolls and have to be unrolled and placed to lie in the pond, lagoon or storage space. With the base (20) (23) made from high density polyethylene the McGROARTY material is less flexible that when using a fabric (non-woven or woven) for the base. This means that the product is much more difficult to handle and the montmorillonite is likely to crack during folding and unfolding. Further, because of the nature of an HDPE plastic sheet the adhering of the montmorillonite to its surface is not easy. Quite large quantities of very strong glue have to be used. As mentioned, in the McGROARTY construction the montmorillonite particles or granules are applied in layers which are adhered not only to the base but also to each other. This makes the product even less flexible and more difficult to handle. Because of the high stiffness of the product McGROARTY has to dispense with any scrim such as the scrim (15) (18) and this means that if any montmorillonite is loosened due to folding and unfolding it can easily become displaced leaving voids in the montmorillonite layer. The McGROARTY material is also very stiff and difficult to handle.

A further waterproofing barrier material is disclosed in British patent number 2 202 185 (NAUE). In the NAUE specification a layer of montmorillonite is sandwiched between a pair of layers of non-woven textile material, in which two layers are united by needling, the needles passing through the layer of montmorillonite and uniting all three layers. This product again has disadvantages. Firstly, both the non-woven layers of textile material are essentially gas venting. Therefore, when they are laid they have the same disadvantages as the CLEM construction. Further, because the montmorillonite is not adhered to the layers, as the material is unfolded, folded and manhandled during installation, the montmorillonite can move relative to the two layers leaving voids and/or more permeable thinner areas in the montmorillonite layer.

There is a further disadvantage in that all these earlier materials tend to use particulate montmorillonite which may be from 2 - 5, usually about 3mm in size. Although finer material can be poured to fill gaps between the larger granules, such granules tend to make up the bulk of the montmorillonite layer in the waterproofing material. As the water proofing material is only relatively thin, for example containing only perhaps one or two layers of montmorillonite granules, problems can arise in connection with foreign bodies in the montmorillonite used. In its natural state montmorillonite is found alongside shale and other impurities. Whilst the montmorillonite can be quite highly purified, it is not unusual for a low percentage of shale particles to remain in the final sized and graded montmorillonite. An unfortunate result of the use of relatively large granules of montmorillonite in the layer is that granules of impurities can also become incorporated in the material. The chemical nature of shale and some other impurities have the effect that not only are they not montmorillonite (and therefore do not swell upon contact with water), but, when wetted, act as to inhibit swelling in adjacent montmorillonite granules. Thus, a single granule of shale in a layer of waterproofing material can form a small area (perhaps 10mm in diameter) which does not swell upon being contacted with water. Small such areas are generally water impermeable, but medium and larger such areas allow water to pass through the sheet. When water pressure is high this flow can cause significant wash out of adjacent montmorillonite leading to failure of the sealing system. Although the percentage of impurities is small, and although the failure rate is small, when a large area is sealed using sheet material incorporating such impurities it needs only a single leak for the whole system to have failed. A pond or lagoon which has a single leak is no pond or lagoon at all!

Particulate montmorillonite has also been mixed with various organic components to form a thick putty (see US Patent Number 4 534 925). Typical components are polypropene and polybutene. This material has been extruded in the form of rods and sheets, usually being stored between layers of release paper. Such material has been used for sealing ground foundations and similar structures. It has not, however, being extruded so as to become united with a carrier sheet and be capable of use in large rolls for covering large areas. Indeed, the polypropene and polybutene used is intended deliberately to give the extruded material a rubbery or formable consistency enabling it to be moulded by hand around small areas such as chimneys, at joints in concrete panels or where drains penetrate foundations. These materials are also quite expensive and prohibitively so for use in relation to large area sheets.

~~It is an object of the present invention to provide a waterproofing material whereby the above described disadvantages are reduced or minimised.~~

Smectite includes montmorillonite (dioctahedral) and saponite (trioctahedral) clay minerals and their chemical varieties. They have commercially valuable swelling and ion-exchange properties.

AUSTRALIAN PATENT OFFICE
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The smectites have a layer ~~of~~ lattice structure, but differ from micas in that the bonds between layers are weakened because of internal chemical substitutions. Montmorillonite consists of layers of negatively charged oxygen (O) atoms within which several types of positively-charged cations are fixed in specific positions. In a two dimensional schematic diagram of the structure (figure 11), four layers of oxygen atoms can be seen to define upper and lower tetrahedral sheets containing tetravalent silicon (Si) and sometimes trivalent cations (3+) of aluminium (Al) and iron (Fe). The apices of the tetrahedra point toward each other and oxygen atoms at the apices form part of the octahedral sheet that may contain trivalent cations (Al, Fe), divalent cations (Fe, Mg), both divalent (+2) and trivalent cations, or divalent and monovalent (+1) lithium (Li) cations. The presence of two tetrahedral sheets and one octahedral sheet is the basis for classifying the montmorillonite structure as 2.1 (2x tetrahedral 1 x octahedral sheet structure). The 2.1 structural units are separated by interlayers of loosely held hydrated cations. These cations are present to balance the negatively charged structure.

If a particle of Montmorillonite is to expand it needs to take in water into its interlayers. This mechanism is valency dependent. Ionic compounds are formed because a metal atom donates one or two electrons to a non-metal atom (or acid radical group). For example, in table salt (sodium chloride), the

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electron from the highest energy level in the sodium atom is donated to the chlorine atom and they both form ions a sodium one plus cation and chloride one minus anion. The higher the valency the shorter the bond length the more stable is the montmorillonite, ie calcium two plus cations will replace sodium one plus cations. In order for this replacement to take place the cation must get close enough to the montmorillonite substrate, to do this other mechanisms must be considered.

If a particle of montmorillonite is dropped into a beaker of water its interlayers take in water, and gradually the clay spreads until eventually it is uniformly distributed. What causes montmorillonite molecules to behave this way? The answer depends on the fact that the molecules within the interlayers are in a state of random motion. Although they can move in any direction, the fact that initially (wetting of the particle) there are far more molecules in the immediate vicinity of the interlayers increases the probability of their moving away from each other resulting in expansion. This process is diffusion, and is defined in this instance as a movement of molecules from a region where they are at a comparatively high concentration (dry) to a region where they are at a lower concentration (hydration) giving a volume increase. Diffusion will always proceed whenever such a concentration gradient exists, and it will continue until eventually the molecules are uniformally distributed and lattice stabilisation is achieved, at which time equilibrium is said to be reached.

Osmosis for the present purpose can be regarded as a special case of diffusion; the diffusion of water from a weaker to a stronger concentration. A weak solution of table salt, for example, will contain relatively less salt and more water than a strong solution of salt. Thus the concentration gradient is from the weak to the strong solution. If two such solutions were in contact, the water molecules would move one way and the salt molecules the other until both were uniformly distributed (equilibrium). If, however, the two solutions are separated by a membrane which allows water but not salt to pass through, only water can diffuse. Such a membrane is said to be selectively permeable or "semi permeable" and the water movement is called osmosis, and is defined in this instance as the movement of a solvent (water) across a selectively permeable interface (membrane) from a weak to a strong concentration of ions in solution. Montmorillonite interlayers are water selective due to the attraction of dipolar water molecules to the highly charged clay particles.

As has been discussed above, the montmorillonite clay is made up of a plurality of structural plates each of which has four layers of oxygen atoms. The outer layer of each plate has a generally tetrahedral format and presents a surface to the interlayer to which cations are loosely bonded. In sodium montmorillonite which is a popular and useful material the cations are sodium ions and are connected to the tetrahedral layers by relatively weak Van Der Waal bonds. The interlayers contain a certain amount of hydrating water molecules. When the montmorillonite is contacted with water more water enters the interlayer, being attracted to the charged cations in the interlayer and moving by diffusion and capillary reaction so as to increase the thickness of the interlayer. If a body of montmorillonite is confined between a pair of relatively immobile surfaces the pressure within it upon contact with water can become so high such as to prevent any further movement of water into the structure. This build up of a high pressure layer which cannot absorb any water makes montmorillonite an excellent water-proofing agent. It is widely used in civil engineering structures.

Often used as a substitute for sodium montmorillonite is calcium montmorillonite wherein the loosely held cations in the interlayer are mainly Ca 2+ rather than Na -. Because of their divalancy the calcium ions bind more strongly to the outer tetrahedral layers than does sodium. In use calcium bentonite has a property that when initially wetted it will swell and expand in the same way as sodium montmorillonite. However, if the material should dry out, for example due to low rain fall or a falling water table calcium montmorillonite cannot shrink back to its original size upon loss of water without cracking. After cracking and upon re-wetting the interlayer becomes incapable of absorbing more water and therefore the clay can not re-wet so as to reform the water proof barrier. Thus, a calcium bentonite water proofing material should only be used in cases where permanent wetness is to be encountered. It is possible to treat calcium bentonite with a strong sodium containing solution so as to displace a certain percentage of the calcium ions from the interlayer and replace them with sodium so as to give the calcium montmorillonite properties closer to sodium montmorillonite. However, this material is not as good as pure sodium montmorillonite, and tends to suffer from the same problems as calcium montmorillonite.

All sodium containing montmorillonites do have a problem when the water which comes into contact with them is contaminated by salts, particularly sea water or other salts which render the ground water ionised and highly active. In ground water calcium is invariably present in quantity from soil and minerals. When such ionic calcium comes into contact with montmorillonite it invariably tends to migrate into the interlayers. Once in the interlayer the double valency of the Ca^{+} cations makes the calcium selectively adhere to the four sides of the tetredral layers displacing sodium. Such contamination can quite quickly result in complete stripping of sodium from the interlayer, so converting the montmorillonite from the sodium to the calcium form with the disadvantage which has been outlined above.

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This particular process makes it generally unwise to use even sodium montmorillonite in a situation where the ground water can become rapidly ionised or contaminated by leachates or the like. In particular, fertilisers are a particularly notorious cause of ground water ionisation and can cause sodium montmorillonite break down.

In a paper entitled "Preparation of Montmorillonite - Polyacrylate Intercalation Compounds and the Water Absorbing Property" by Ogawa *et al* published in Clay Science Number 7, 243 251 (1989), the authors have described the introduction of an acrylamide into montmorillonite and the polymerisation of the acrylamide to form a polyacrylamide intercalation compound. The enhanced water-absorbing properties of the compound are noted.

It is to be appreciated, of course, that the processes carried out in the Ogawa paper were essentially laboratory processes involving small amounts of material. No techniques were described for making any useful product and there was not discussion of the advantages of high density such compounds as waterproofing agents.

According to the present invention there is provided a waterproofing laminate comprising a support sheet united with a waterproofing layer, said waterproofing layer being formed from a plastic mass containing particulate smectite clay mixed with liquid, at least a portion of said liquid being water.

Desirably, the waterproofing layer is sandwiched between the support sheet and a cover sheet. Reinforcement may be provided in the waterproofing layer. The reinforcement may be secured to the aforementioned cover sheet and/or the support sheet.

The invention also provides a method of making a waterproofing laminate comprising mixing

AUSTRALIAN PATENT OFFICE

particulate smectite clay with liquid, at least a portion of which is water, kneading the mixture to form a plastic mass, forming the plastic mass into a continuous waterproofing layer and uniting said layer with a support sheet.

The waterproofing layer united with the support sheet can be treated to cause the layer to loose a degree of plasticity. This may enable the laminate to be handled and stored without undergoing further deformation. The treatment may comprise subjecting the waterproofing layer to a drying step, for example by passing the waterproofing laminate through an oven, to remove liquid from the layer by evaporation. This may further increase the swellability of the smectite upon contact with water in use.

Desirably, the smectite clay is mixed primarily with water to form a paste or a putty-like plastic mass which can be extruded, rolled or otherwise formed into the continuous layer.

The liquid may optionally contain a carboxymethyl cellulose (CMC) compound.

Additives which modify the behaviour of the smectite under certain specified conditions such as salt water, or presence of strong leachates, radiation hydrocarbons or organic chemicals can be added at the mixing stage to be operative when the smectite is in use.

Union of the waterproofing layer with the support sheet can be by adhesive, but desirably no adhesive is used, the mixture of smectite and water (and any other substance(s)) being such as to allow pressure to force the plastic mass into interstices of the support sheet (which is desirably of a textile nature) physically to unite the two. Similar connection can be effected beween the layer and the aforementioned cover sheet.

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In addition to water and, optionally, CMC, organic materials such as methanol, ethanol propanol and other alcohols, preferably upto C_{12}, glycerine, diesel and other oils and fats can be used. These materials do have the advantage that it is not necessary to drive off so much water so as to increase the swellability of the smectite layer, but they also have the disadvantages that they do need a drying step so that

AUSTRALIAN PATENT OFFICE

the material is not subject to further deformation under its own weight during storage and transportation and many organic materials are usually far more expensive then water.

Alcohols, particularly methyl alcohol do, however, have particular advantages. Whilst alcohols are generally expensive, they are also usually far more volatile than water. Thus, a plastic mass made using methyl alcohol can, after having been formed into a cohesive continuous layer be dried using far less heat than would be necessary to drive out the water from a similar mass. In addition to this however, the alcohol driven off can be condensed and reused thus offsetting the cost thereof.

The montmorillonite mesh size can be anything from 50 mesh or smaller, desirably, however the size is a maximum of 100. In practice a mesh size of 200 has been found useful although variations downwards from about 100 mesh do work although with less desirable qualities. Finer meshes are perfectly acceptable, but tend to be unnecessary. The smectite used is desirably sodium montmorillonite although calcium montmorillonite (modified by treatment with sodium hydroxide) can be used. As the montmorillonite is usually broken down significantly during mixing to micro sizes, initial grain size is not critical.

~~The~~ Fabrics used as support and/or cover layer can be conventional woven or non-woven textiles such as nylon or

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polypropylene or polyester. They should be non-venting (that is to say they do not allow gas or liquid to pass along the structure in use to any significant degree). The fabrics are desirably woven and this degree of non-venting can be achieved by ensuring that the fabric is of relatively open mesh and fairly thin, a significant portion thereof being embedded in and physically uniting with the outer layer of the montmorillonite layer.

~~The invention includes of course, a waterproofing sheet made by the methods aforesaid.~~

Apparatus for making such a waterproofing ~~material~~ laminate includes a conveyor, means for feeding a support to the conveyor, means for applying a plastic smectite-containing mass onto the support, and means for forming said plastic mass into a uniform continuous layer.

Means can be provided for sizing the laminate in thickness and/or in width.

Desirably the apparatus includes means for conditioning the laminate after formation to render it stable in use and storage. Said means can include an oven for evaporating substances, from the laminate.

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Means for supplying the plastic mass to the conveyor can include one or more nozzles, and/or an extrusion head.

Means can also be provided for supplying a cover sheet to a surface of the layer remote from the support sheet.

Means can also be provided for feeding a reinforcement to be embedded within the smectite containing layer.

Means can be provided for uniting said reinforcement with one or both of the cover and support sheets; for example by heat sealing.

The invention also provides a method of waterproofing a structure to prevent ingress and/or egress of aqueous fluids including the steps of providing a plurality of sheets each in the form of a laminate of a support sheet and a layer of cohesive smectite, formed from a plastic mass, as aforesaid, laying the sheets to cover the surface of said article in overlapping relationship and protecting said sheets against accidental damage in use.

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Waterproofing material in accordance with the invention can be used, for example, as roofing material or to provide a seal for a pipe or other plumbing fittings.

The smectite mixture can be in the form of a sealing ring or annulus or can be provided as a continuous length for wrapping around joints. The sealing material can be made by the aforesaid methods of forming a plastic mass and extruding, cutting or moulding therefrom.

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The plastic mass advantageously contains a smectite/liner intercalation complex.

The liner can closely bind sodium cations to the outer layers of plates of the smectite structure, therefore reducing the possibility of their replacement by calcium cations.

Alternatively the lining can replace the sodium cations leaving a generally neutral face which can absorb water by capillary action, but which is generally neutral and therefore does not attract calcium cations.

The liner used will normally be an organic compound compatible with the outer layers of the smectite plates. Suitable compounds can be sugars such as fructose, glucose, dextrose and the like which have comparable molecular shapes and will complex with the tetrahedral layers on the outside of the plate.

A further and desired liner is an acrylate. The material can be added as the polyacrylate or an acrylation process can be carried out in contact with the clay. The acrylate can have the formula shown in figure 12. Although the sodium salt of polyacrylate is shown, other cation forms can be used. In the sodium cation form, the acrylate can replace the sodium cations which normally coat the outer layers of the smectite plates.

The acrylate polymer may be doped with various desirable materials to alter various properties of the clay. One particular doping agent is glycerol. The introduction of glycerol can increase the flexibility of the clay so that a length of the clay can be bent easily without breaking.

Methanol can also be introduced, as previously mentioned. Methanol is a useful material for increasing the flexibility and reducing the stiffness of the mixture thus assisting in its processing.

A further problem of smectite clay when used as a waterproofing material, is that its function

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is very dependent on the amount of montmorillonite used. For example when a body of a montmorillonite is constrained between two surfaces, such as the concrete of a structure and the ground, when contacted by water it swells and forms the aforesaid high pressure layer which prevents ingress of water to the structure and therefore effectively waterproofs it. To increase the waterproofing efficiency of the clay body, larger quantities of montmorillonite can be used. However, higher quantities of montmorillonite mean thicker sheets of material which are more difficult to handle and which are heavier, have more transportation costs and are bulky. In sheets which consist principally of particulate montmorillonite there can be significant difficulty in getting a large quantity into a small area. Sheet material used for waterproofing in ground situation or for roofs, walls and the like tend to have relatively low densities. This is because they are generally made from particulate montmorillonite adhered to a supporting sheet as of plastics material or textile material and secured thereto by a variety of means ranging from adhesive to needling to sewing or by embedment in a mesh of fibres.

In a preferred embodiment, the smectite clay waterproofing material has a density greater than 1000 kg m^{-3}.

The waterproofing material may be formed into a sheet at least a metre wide, and desirably up to four metres wide or more.

Preferably, the plastic mass is exposed to suction to remove gas. The suction may be applied during mixing or kneading, or may be applied to the waterproofing layer after it has been formed.

Desirably the degassed material is subsequently subjected to pressure. Advantageously, this reduces the number of voids in the product as well as urging the molecules of the product closer together to produce a denser product.

The pressure can be applied by extrusion or by passing the forming material through rollers, or by any other convenient means.

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Where the product is subjected to pressure as aforesaid, it is desirable that the pressure is applied when the temperature is within the range of 15 to 30° C.

A further disadvantage of existing smectite-based waterproofing materials is that upon exposure to water they tend to swell (this is the very factor which gives them their waterproofing properties in that they produce an area of such high pressure that additional water cannot penetrate). However, the pressures can tend to be very high and, therefore, a very significant overlay of either a heavy earth layer (for example one to two metres) or up to 3" or more of concrete are necessary in order that the expansion pressure of the smectite cannot cause movement or displacement of any structure.

The invention advantageously provides a waterproofing material having a significantly reduced expansion pressure compared with known smectite based waterproofing material.

The expansion pressure can be as low as 10mm of concrete as carried out in the test later defined herein.

Preferred embodiments of the laminate of the invention provide a barrier against aggressive ionic fluid, the barrier being in the form of the constrained waterproofing layer, wherein interlayers of the smectite have been treated with acrylate or polyacrylate or comparable substances.

The interlayers are then advantageously capable of absorbing water to swell the material to a barrier pressure whilst the acrylate or polyacrylate inhibit ion exchange between said fluid and the smectite.

The fluid will normally be aqueous and can be highly ionised fluid such as leachate or fluid containing fertilizer and the like. However, the barrier can be equally effective against organic fluids or fluids containing organic material, as the smectite interlayers remain proof against ion exchange with such fluid.

AUSTRALIAN PATENT OFFICE

The waterproofing layer needs to be constrained in order that the barrier pressure can be achieved. The constraint can be a back-fill or overlay of earth or other material or, in solid structures, an adjacent or surrounding area of concrete or the like can be used.

A further problem with known smectite based waterproofing materials is that it has been very difficult to secure them to surfaces to be waterproofed. Whilst a flat or gradually sloping surface can be easily waterproofed simply by laying a sheet of the smectite material thereon, when vertical surfaces (such as adjacent edges of concrete panels) are to be waterproofed it has been necessary somehow to attach a smectite based strip thereto. Existing methods used have included the provision of rebates into which strips of seal material can be pushed and the use of clips or nails. Although nails can be used they tend to be frowned upon as they pierce a waterproof layer and they can introduce metal ions into the surrounding water which may have a detrimental effect. Because of the generally incohesive nature of clays and their friability, adhesives have not been very effective. Some heavy soaking adhesives have been used, particularly the type of adhesive used in the adherence of smectite particles to sheets. However these adhesives have a great tendency to inhibit the swelling properties of the clay and to react adversely.

Preferred embodiments of the material of the invention are readily securable to a surface using an adhesive compatible to the aforementioned acrylate or polyacrylate component, such as a cyano acrylate adhesive.

The invention will be described further, by way of example, with reference to the accompanying drawings wherein;

Figures 1 and 2 are cross sectional views illustrating overlap joints in the prior art and their disadvantages;

Figure 3 is a cross sectional view illustrating a preferred waterproofing material of the invention;

AUSTRALIAN PATENT OFFICE

Figure 4 is an enlarged cross sectional view illustrating a surface of a preferred material of the invention;

Figure 5 is a schematic view illustrating the apparatus of the invention suitable for carrying out a preferred method of the invention;

Figure 6 is a plan view of part of the apparatus of figure 5 and illustrating two possible variations;

Figure 7 is a view similar to figure 3 but illustrating a modified material of the invention;

Figure 8 is a view similar to figure 7 but illustrating a still further modified material;

Figure 9 is a view comparable to figure 1, but illustrating an overlap join made using the material of the present invention;

Figure 10 is an enlarged view of the portion ringed at numeral 10 in figure 9.

Figure 11 is a basic two dimensional sketch illustrating structure of montmorillonite;

Figure 12 is a chemical formula illustrating the structure of an

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acrylate useable in the invention;

Figure 13 is an enlarged view illustrating the structure of montmorillonite;

Figure 14 is attempted three dimensional representation of montmorillonite after acrylation;

Figure 15 is a view similar to figure 14 but illustrating the addition of doping elements; and

Figure 16 is a view similar to figure 15 but illustrating the microscopic effects of the acrylation.

Referring to figure 3, the waterproofing material (10) is a laminate consisting of a core layer (11) containing montmorillonite. The core layer (11) is united with a support sheet (12) and is desirably but not essentially overlaid by a cover sheet (13).

The features of the material (10) will probably be best apparent from a detailed description of the way it is made and the apparatus which is used to make it.

Referring, therefore, to figure 5 it will be seen that a

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preferred apparatus 54 ~~(14)~~ of the invention comprises a conveyor (15) having an upper run (16) and a lower run (17) entrained about end rollers (18) and (19). The upper run (16) travels from left to right in figure 5.

At the upstream end of run (16) a support sheet (20) is fed from a supply roll (21) by a guide roll (22) so as to run on and in synchronism with the conveyor (16).

The support sheet (20) is a sheet of woven or non-woven textile material (preferably woven) which is relatively loose weave, being quite porous in a direction transverse to its plane.

The web forming the support sheet can be made of any geotextile material which is suitable for disposal within the ground for long periods. Typical materials for weaving or forming the fabric of the sheet (20) can be polypropylene, polyesters including nylon, and many other plastics materials alone or in blends. The material should be sufficiently strong to support the composite laminate to be formed and can be similar to many of the facing sheets used in relation to the prior known materials discussed in the introduction hereto. Polypropylene and cotton mixers can also be used. A typical support and/or cover sheet can be of a print weave and of a weight 700g per sq.metre.

Downstream of the supply roll is a hopper mixer (23) in which

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particulate montmorillonite can be supplied as indicated by the arrow (24). The particulate montmorillonite can be supplied from a mill or like supply and in the preferred embodiment is of 200 mesh. Finer mesh can be used although great advantages are not obtained. Meshes up to 50 mesh can be used, but at sizes greater then 100 mesh, union between the montmorillonite particles is less effective.

The process which takes place in the hopper mixer (23) can be either a continuous or a batch process. Within the hopper mixer (23) a measured quantity of montmorillonite is mixed with a measured quantity of one or more other substances to produce a fluent mass. The other substance(s) can be supplied from a tank or comparable supply (25). The substance(s) (26) will normally be fluid and when mixed with the montmorillonite will form a shapable mass. A liquid used can be an organic liquid such as glycerine, diesel oil or comparable oils or mixes thereof, gels and other plastic or deformable mass-forming substances. However, for economy and for ease of handling and simplicity the desired substance is water. In the preferred embodiment of method of the invention water is mixed with the montmorillonite there being approximately from 10 to 30% water, desirably about 15 to 20%.

Alternatively or liquid such as alcohol can be used. Methyl, ethyl or propyl alcohol can be used. Methyl is preferred. It

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In making a product in accordance with a preferred embodiment of the invention 5 kilograms of montmorillonite were mixed with 0.446 kilograms of sodium carboxymethyl cellulose (CMC), 2.5 litres of methanol and 1.8 litres of water. Both the CMC and the methanol make the mixed and kneaded product more flexible and extrudable. The more water that is used the more heat is required to drive it out. This means added expense.

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means added expense.

Although the above particular mixtures have proved suitable many variations can be made.

Methanol alone or water alone can be used, but neither of these is satisfactory.

The material desirably contains a bulking agent, an anti fungicidal preserving agent, to prevent growth of mould in or on the material and desirably a lubricant to assist in the extrusion process and convey also a degree of flexibility to the plastic mass. CMC is a very desirable substance in that it provides all these properties. It has anti fungicidal properties, it is a lubricant and it makes the product more flexible. It also has the great advantage that upon contact by water, in use, it dissolves. Those areas of the outer surface of the material when first contacted by water have the CMC dissolved out of them leaving micro pores into which more water can penetrate, wash out more CMC and cause rapid expansion of the adjacent montmorillonite. This greatly increases the rate of

water transfer into the material. A bulking agent which dissolves in water and aids water ingress to the montmorillonite is very desirable.

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Instead of being provided by a single material these properties can be provided by other materials. Although many synthetic materials do have these properties, they tend to be expensive and simple plant extracts which are much cheaper are desired. As a bulking agent/lubricant guargum can be used or starch. In connection with these two materials a separate preservative such as any conventional anti fungicidal or micro agent would have to be used.

Any convenient liquid alcohol can be used having from 1 to 12 carbon atoms. Above the 12 alcohols tend to be too viscose for use but below that number any convenient alcohol can be used. It is expected, however, that methyl alcohol will be used because of its cheapness and easy availability. The CC can be in the form of sodium carboxy methyl cellulose or any other convenient compound thereof. Protection against bacterial attack is important because the bacterial reactions can produce hydro carbons which react with the sodium irons in the clay. This can reduce the swellability of the clay.

As a possible variation a soluble coating can be provided to surround a body of material of the invention. This can be arranged to degrade over a relatively short period of time (such as a week). This would enable block seals and the like to be installed without becoming greasy and unhandlable due to adverse weather conditions, but would not affect the function of material

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to swell in use after a brief period of time.

The montmorillonite used is desirably sodium montmorillonite but calcium montmorillonite or treated calcium montmorillonite (and other smectites) can also be used. As shown the materials are first mixed by means of a mixer (27) and then extruded by screws (28), where to ~~an extrusion nozzle~~ (29), where the fluid mass is spread out as a thin layer covering the entire width of the conveyor run (16).

If the reinforcement is required within the montmorillonite layer in order that it can be laid on steep slopes without loss of function it can be desirable to incorporate within the plastic mass a reinforcing layer. This can be done by embedding the reinforcing layer into the mass as it is being extruded or it is being spread out into a layer. The reinforcing layer can be made in the form of a core having bristles or comparable formations extending outwards which, with the core disposed centrally in the body of montmorillonite extend to the surface thereof and contact and possibly project through the surface layers. The material of the reinforcement and the surface layers can be made such that the exposed bristles can be heat sealed to contact and be secured to the outer layers. It is envisaged that it would be possible for the montmorillonite mass to be extruded or formed into a pair of sheets and the reinforcement ~~feed~~ fed between them and to have its bristles projecting through each of the two part layers of the montmorillonite core and project to the other surfaces thereof

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and be united with the support/cover sheets.

Although the extrusion of a thin layer of the plastic mass containing montmorillonite is desirable, as it can be 3 or more metres wide, it could well be that a three metre wide extrusion nozzle is either expensive, slow, or requires inordinate amounts of power to be successful. Such ~~a~~ an extrusion nozzle (29) is shown in figure 5 which also shows an alternative which will be described later.

It is expected that the mass will be extruded as a rod and rolled flat.

Downstream of the nozzle (29) the layer (30) of montmorillonite containing plastic mass is levelled and formed into a uniform uninterrupted layer. This can be achieved by means of an initial doctor blade (31) or more likely, a roller, and subsequent sizing rollers (32) to (34). The pairs of sizing rolls (32) (33) (34) can effect kneading and levelling of the fluid material and subsequent size thickness reductions.

Figure 6 shows one of the rollers and shows the plastics material extruded outwards beyond the edge of the conveyor and being removed by trimming knives (36).

At one of the sets of rollers (32) (33) (34) there is fed a web of cover sheet (37), from a supply roll (38). Of course, if roll

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(32) or (33) and (34) are needed to effect creation of a uniform flat layer of the montmorillonite containing mass, application of the cover sheet (37) can be left until roll (34). However, this is not desirable as rollers (32) and (33) are best protected from the plastic montmorillonite layer by the cover sheet (37).

The liquid which converts the powdered montmorillonite into a plastic fluent mass will need some degree of subsequent treatment, for example by evaporation, drying or partial chemical change so as to ensure that the final material cannot deform further in use or in storage. This can be effected by means of a treatment facility indicated by the reference numeral (39).

In the illustrated apparatus the treatment facility (39) is in the form of an oven which will reduce the solvent water content of the montmorillonite containing layer from 20% down to 5% or less. Hot air is supplied at an inlet (41) and leaves via an outlet (42).

After leaving the treatment facility (39) the laminate can be allowed to cool and then be fed to a store roll (44). A knife or the like can be provided for cutting the laminate as it leaves the oven when the roll (44) is full.

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The initial consistency ~~product, the consistency~~ of the plastic/fluent mass containing montmorillonite can vary widely from almost a liquid condition to a stiff paste. ~~When water is used,~~ The stiffer the paste the better as water has to be expelled by passage through the oven. Again, in the case of organic or organic-containing mixture substances the stiffer the material the less later treatment is necessary to render the final laminate stable and non-deformable during transportation and storage and use. This process will usually involve evaporation comparable to oven drying or a chemical treatment.

As has previously been mentioned the use of a very wide extrusion nozzle (29) may not be practical in view of the power required for such a device. Instead, as illustrated in figure 6 a smaller extrusion or fluid delivery nozzle (45) can be used which can be mounted so as to perform a generally sinuous path transversely of the direction of travel of the run (17) of the belt (15). Thus, the nozzle (45) can follow a path indicated by the line (46). By altering the speed of travel of the nozzle and/or the rate of delivery of the fluent material can be assured that sufficient material is applied to the belt to allow a layer of desired thickness to be formed throughout the area of the belt without voids, cracks or the like which would be most undesirable. To this end it is advantageous if the material can be applied to some significant access and after having been formed into a uniform coherent layer excess material extruded

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Although the above particular mixtures have proved suitable many variations can be made.

The material desirably contains a bulking agent, an anti fungicidal preserving agent, to prevent growth of mould in or on the material and desirably a lubricant to assist in the extrusion process and convey also a degree of flexibility to the plastic mass. CMC is a very desirable substance in that it provides all these properties. It has anti fungicidal properties, it is a lubricant and it makes the product more flexible. It also has the great advantage that upon contact by water, in use, it dissolves. Those areas of the outer surface of the material when first contacted by water have the CMC dissolved out of them leaving micro pores into which more water can penetrate, wash out more CMC and cause rapid expansion of the adjacent montmorillonite. This greatly increases the rate of

water transfer into the material. A bulking agent which dissolves in water and aids water ingress to the montmorillonite is very desirable.

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As previously mentioned, any suitable ~~Any convenient~~ liquid alcohol can be used having from 1 to 12 carbon atoms. Above ~~the~~ C 12 alcohols tend to be too viscose for use but below that number any convenient alcohol can be used. It is expected, however, that methyl alcohol will be used because of its cheapness and easy availability. The CMC can be in the form of sodium carboxy methyl cellulose or any other convenient compound thereof. Protection against bacterial attack is important because the bacterial reactions can produce hydro carbons which react with the sodium irons in the clay. This can reduce the swellability of the clay.

As a possible variation a soluble coating can be provided to surround a body of material of the invention. This can be arranged to degrade over a relatively short period of time (such as a week). This would enable block seals and the like to be installed without becoming greasy and unhandlable due to adverse weather conditions, but would not affect the function of material

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to swell in use after a brief period of time.

The montmorillonite used is desirably sodium montmorillonite ~~and~~, but calcium montmorillonite or treated calcium montmorillonite and other smectites can also be used. As shown the materials are first mixed by means of a mixer (27) and then extruded by screws (28) to an extrusion nozzle (29). Where the fluid mass is spread out as a thin layer covering the entire width of the conveyor run (16).

If reinforcement is required within the montmorillonite layer in order that it can be laid on steep slopes without loss of function it can be desirable to incorporate within the plastic mass a reinforcing layer. This can be done by embedding the reinforcing layer into the mass as it is being extruded or as it is being spread out into a layer. The reinforcing layer can be made in the form of a core having bristles or comparable formations extending outwards which, with the core disposed centrally in the body of montmorillonite extend to the surface thereof and contact and possibly project through the surface layers. The material of the reinforcement and the surface layers can be made such that the exposed bristles can be heat sealed to contact and be secured to the outer layers. It is envisaged that it would be possible for the montmorillonite mass to be extruded or formed into a pair of sheets and the reinforcement feed between them and to have its bristles projecting through each of the two part layers of the montmorillonite core and project to the other surfaces thereof

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On the microscopic scale (which is illustrated very schematically in figure 16) a particle of clay consists of a plurality of small structural plates between which the helical acrylate molecules are disposed. The surfaces of the helical acrylate molecules are bonded to the tetrahedra within the faces of the structure plates opposite the interlayers and project beyond the edges of the particle. This projection of the acrylate molecules beyond the surface of the particle has a significant effect in the absorption of water by the clay. Thus although the acrylate does, to some extent mask the electro-chemical water absorbing properties of the clay by effectively neutralising the sodium cations in the interlayer the extending helical polyacrylate molecules extending outwardly from the particles have a surface tension effect which draws water towards the particles and causes it to enter into the interlayers by capillary action thus causing a swelling of the particle which is comparable to the electro-chemical swelling which previously occurred but which is not dependent on the presence of cations within the interlayers.

This has the important effect that any cations which enter within the interlayer can not replace sodium cations and thus do not reduce the capacity of the clay to expand, shrink and re-expand after drying out.

Alternatively, other materials may be used. For example sugars such as fructose, glucose, dextrose can be used. All act in very similar way to the acrylic molecule and have comparable and similar effects. The use of sugar may, however, be undesirable in some circumstances in view of its encouragement of microbial growth. Of course, there may well be advantages in this particular property in certain situations.

A further alternative material is alkylammonium trimethyl alkyl ammonium which can be used in the manner very similar to the polyacrylic compound to give a similar material with

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similar properties.

In another example of a smectite clay water proofing material, sodium montmorillonite powder was mixed with polyacrylate, glycerol and methanol. The mass was mixed together for some fifteen minutes and then extruded through a 25mm square orifice at a rate of about 0.5 metres per second to produce a rope like concrete sealing strip having a density of about 1350 kg m m^{-3}.

The actual density can be varied by varying the proportion of materials in the complex.

Of course, the waterproofing material can be made without using polyacrylate. In addition it is possible to use CMC either in addition to the acrylate or as a substitute therefore. The CMC can be useful in varying the reaction rate of the clay but it also has a property of forming, on the surface of the extruded material, a layer which improves the life of the sealing material by resisting degradation and swelling by rain over a first few hours or days.

In testing a waterproofing sheet comprising a smectite organic complex as described above, a layer of conventional particulate smectite clay waterproofing sheet was laid on the ground and contacted with typical water high in ionic leaching chemicals. After six hours the bentonite layer had absorbed the liquid and had swelled to form a uniform water retaining layer.

The complex clay sheet described above was similarly treated and had within six hours reached precisely the same condition.

The two sheets were then allowed to dry. In the complex clay sheet, the sheet reduced in

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product, the consistency of the plastic/fluent mass containing montmorillonite can vary widely from almost a liquid condition to a stiff paste. When water is used, the stiffer the paste the better as water has to be expelled by passage through the oven. Again, in the case of organic or organic-containing mixture substances the stiffer the material the less later treatment is necessary to render the final laminate stable and non-deformable during transportation and storage and use. This process will usually involve evaporation comparable to oven drying or a chemical treatment.

As has previously been mentioned the use of a very wide extrusion nozzle (29) may not be practical in view of the power required for such a device. Instead, as illustrated in figure 6 a smaller extrusion or fluid delivery nozzle (45) can be used which can be mounted so as to perform a generally sinuous path transversely of the direction of travel of the run (17) of the belt (15). Thus, the nozzle (45) can follow a path indicated by the line (46). By altering the speed of travel of the nozzle and/or the rate of delivery of the fluent material it can be assured that sufficient material is applied to the belt to allow a layer of desired thickness to be formed throughout the area of the belt without voids, cracks or the like which would be most undesirable. To this end it is advantageous if the material can be applied to some significant excess and after having been formed into a uniform coherent layer excess material extruded

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sideways is removed by means of the trimming knives or the like (36). Of course, such material can be reclaimed and re-used.

It has been mentioned that the support sheet and/or the cover sheet can be of woven or non-woven material. Woven material is preferred as it gives significant strength with lesser weight of material. A non-woven material might have advantage, however, in that it can form a physical union with the montmorillonite containing core (11). The term core (11) is used even though the cover sheet (13) may not be provided.

As best seen in figures 4 and 10 the action of the rollers (32) (33) and (34) is to cause the support/cover sheets (12) (13) to be partially embedded in surface zones of the plastic mass of material forming the core (11) whilst the core is in a plastic state. There is no need for any adhesive, which is an expensive and unreliable component.

As the core is treated in the facility (39) either by evaporation or chemically so as to cause the core to harden there is a physical locking of the surface portions of the core (11) with portions of the fabrics (12) (13) physically uniting them to the surface without the need for adhesive.

This has two important consequences.

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ITEM	PERCENTAGE RANGE
Water	15 - 25
Sodium Polyacrylate	8 - 16
(Methyl) Alcohol	0 - 5
Wyoming Bentonite	50 - 75
Carboxy Methyl Cellulose	0 - 3
Sodium Hexameta Phosphate	0 - 0.5

The alcohol used can be methyl alcohol, ethyl alcohol or any other liquid alcohol and serves to facilitate introduction of the ~~liner~~ polyacrylate into the smectite interlayers. Further, some of the alcohol is, during the heating stage, (the heating is due to the heat of the reaction which begins to effect the material towards the end of the reaction period) ~~is~~ expelled and carries with it

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excess polyacrylate which can be deposited on the outside of the extruded strip as a shiny layer. This layer may serve as lubricant as the strip passes through the die and helps to produce a smooth continuous surface. In addition this deposited acrylate also forms a coating for the material which delays the onset of severe water briefly and helps in allowing the material to be installed and perhaps wetted or exposed to the atmosphere before additional material is applied to the surround.

The function of the pressure during extrusion is to increase the density of the product by eliminating voids which might otherwise form within a less than coherent mass. This, together with the vacuum step which has removed air has the effect of compressing the material to a high density. This moves the molecules slightly closer together during extrusion thus increasing the rate of reaction and encouraging the formation of the complex from the intercalated polyacrylate liner.

Desirably the density is greater than 1,000 kilogrammes per metre cube and a preferred density is over 1,300 kg m^{-3} ~~1,3000 kilogrammes per metre cubic.~~

The process described above produces a sealing strip very suitable for use in concrete foundations and the like and also in plumbing applications in the sealing of pipes and comparable

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from a minimum of 4 up to 10 or 20mm or more in thickness , the length of roll which can be transported is not very high. On large sites the elimination of large amounts of joints and the elimination of road transportation can mean significant cost savings.

The apparatus of the invention can be divided into a number of mobile units, for example the main conveyor, the mixing hopper and the drying could form three separate unit loads.

As is mentioned earlier, the invention envisages the use of a material comprising expandable montmorillonite clay on a flat or slightly slopping roof as the whole or a significant part of the water proofing component thereof. The material of the invention is particularly suitable for this purpose as it can be laid on relatively higher slopes than previously known montmorillonite sheets without them being very expensive. Thus, in the case of a roof which has upstands the montmorillonite sheet of the present invention can be laid to extend not only over the flat surface but also over the upstands to form a water proof layer. The montmorillonite core will normally be overlaid by several cm of gravel or like material providing a bearing layer protecting the montmorillonite beneath. The montmorillonite used will, desirably, be of the sort which can be allowed to dry out and be rewetted repeatedly as this will often happen to a roof structure.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A waterproofing laminate comprising a support sheet united with a waterproofing layer, said waterproofing layer being formed from a plastic mass containing particulate smectite clay mixed with liquid, at least a portion of said liquid being water.

2. A laminate as claimed in claim 1, wherein a portion of said liquid is an alcohol having from 1 to 12 carbon atoms.

3. A laminate as claimed in claim 2, wherein said alcohol is methanol, ethanol or propanol.

4. A laminate as claimed in any preceding claim, wherein said liquid contains acrylate or polyacrylate.

5. A laminate as claimed in any preceding claim, wherein said liquid contains glycerol.

6. A laminate as claimed in any preceding claim, wherein said liquid contains a carboxymethyl cellulose (CMC) compound.

7. A laminate as claimed in any preceding claim, wherein the plastic mass is extruded and/or rolled to sheet form to form the waterproofing layer.

8. A laminate as claimed in any preceding claim, wherein the waterproofing layer is sandwiched between the support sheet and a cover sheet.

9. A laminate as claimed in any preceding claim, wherein reinforcement is provided in the waterproofing layer.

10. A laminate as claimed in claim 9 wherein the reinforcement is secured to the support

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sheet.

11. A laminate as claimed in claim 9 when appended to claim 8, wherein the reinforcement is secured to the cover sheet.

12. A laminate as claimed in any preceding claim, wherein the waterproofing layer has a density greater than 1000kg per cubic metre.

13. A method of making a waterproofing laminate comprising mixing particulate smectite clay with liquid, at least a portion of which is water, kneading the mixture to form a plastic mass, forming the plastic mass into a continuous waterproofing layer and uniting said layer with a support sheet.

14. A method as claimed in claim 13, wherein the plastic mass is extruded and/or rolled into the continuous waterproofing layer.

15. A method as claimed in claim 13 or 14 which comprises treating the waterproofing layer united with the support sheet to cause the layer to lose a degree of plasticity.

16. A method as claimed in claim 15, wherein said treatment comprises subjecting the continuous waterproofing layer to a drying step by passing the waterproofing laminate through an oven to remove liquid from the layer by evaporation.

17. A method as claimed in any one of claims 13 to 16 wherein the continuous waterproofing layer is united with the support sheet by adhesive.

18. A method as claimed in any one of claims 13 to 16 wherein the continuous waterproofing layer and the support sheet are physically united.

19. A method as claimed in any one of claims 13 to 18 wherein alcohol is used as part of

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the liquid.

20. A method as claimed in claim 19 wherein some of the alcohol is removed from the continuous waterproofing layer united with the support sheet, and recycled.

21. A method as claimed in any one of claims 13 to 20, wherein the plastic mass is exposed to suction to remove gas therefrom prior to being formed into said continuous waterproofing layer.

22. A method as claimed in any one of claims 13 to 20, wherein the continuous waterproofing layer is exposed to suction to remove gas therefrom.

23. A method as claimed in claim 21 or claim 22, wherein the degassed plastic mass or continuous waterproofing layer is subjected to pressure.

24. Waterproofing laminate substantially as hereinbefore described with reference to the accompanying drawings but excluding Figures 1 and 2.

25. A method of making a waterproofing laminate substantially as hereinbefore described with reference to the accompanying drawings but excluding Figures 1 and 2.

DATED this 23rd day of December, 1996.

RAWELL GROUP HOLDINGS LIMITED
By its Patent Attorneys
DAVIES COLLISON CAVE

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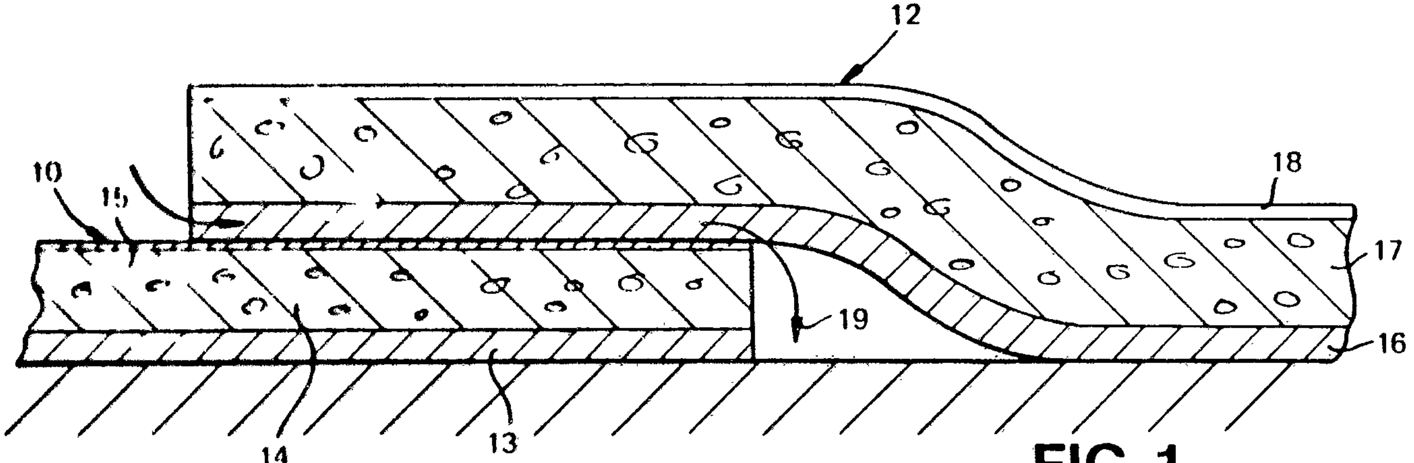

FIG. 1
PRIOR ART

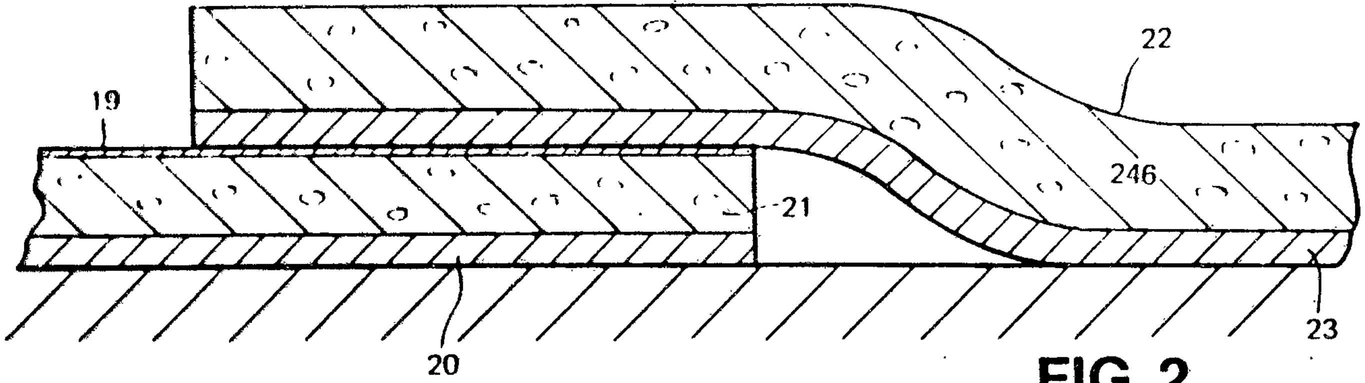

FIG. 2
PRIOR ART

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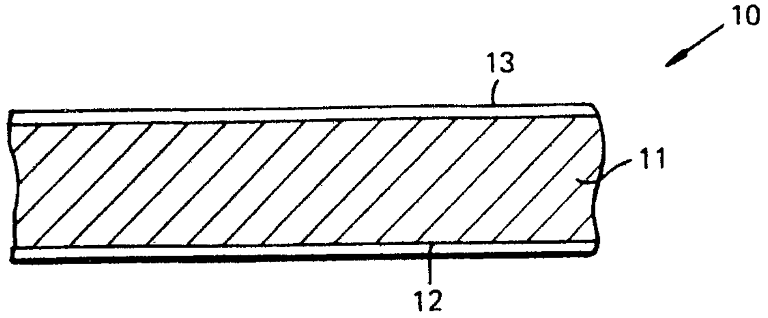

FIG. 3

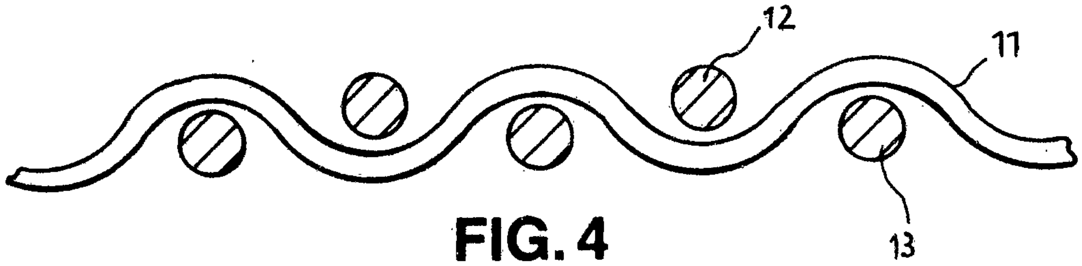

FIG. 4

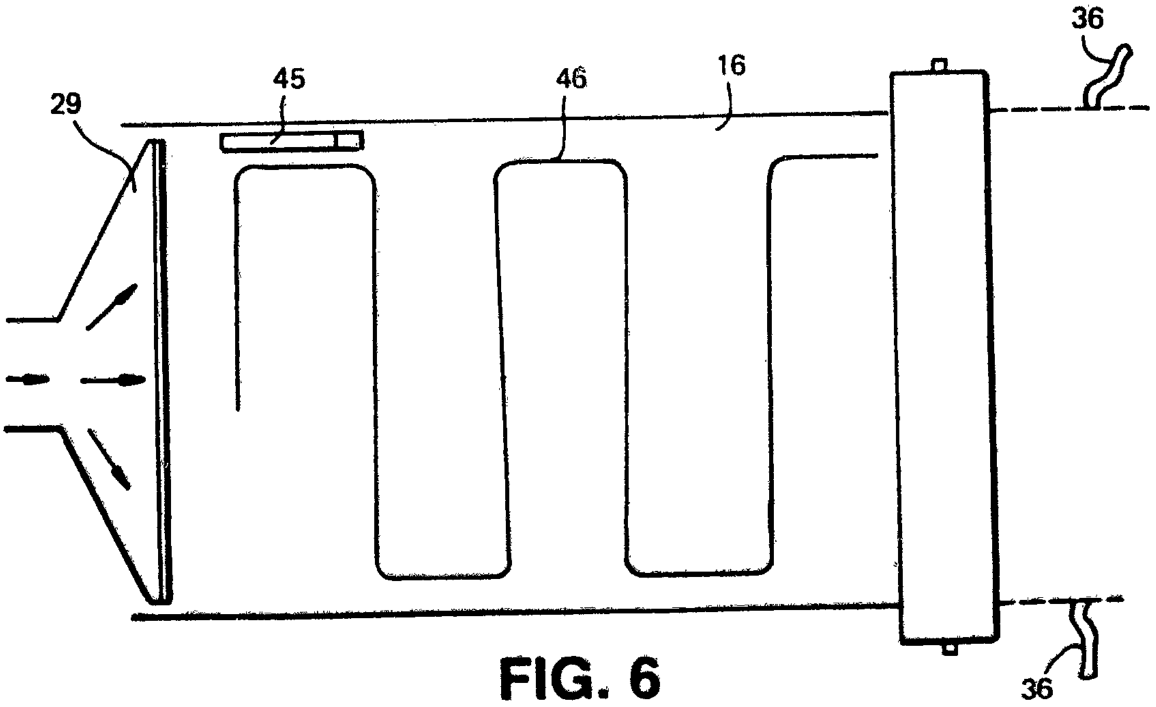

FIG. 6

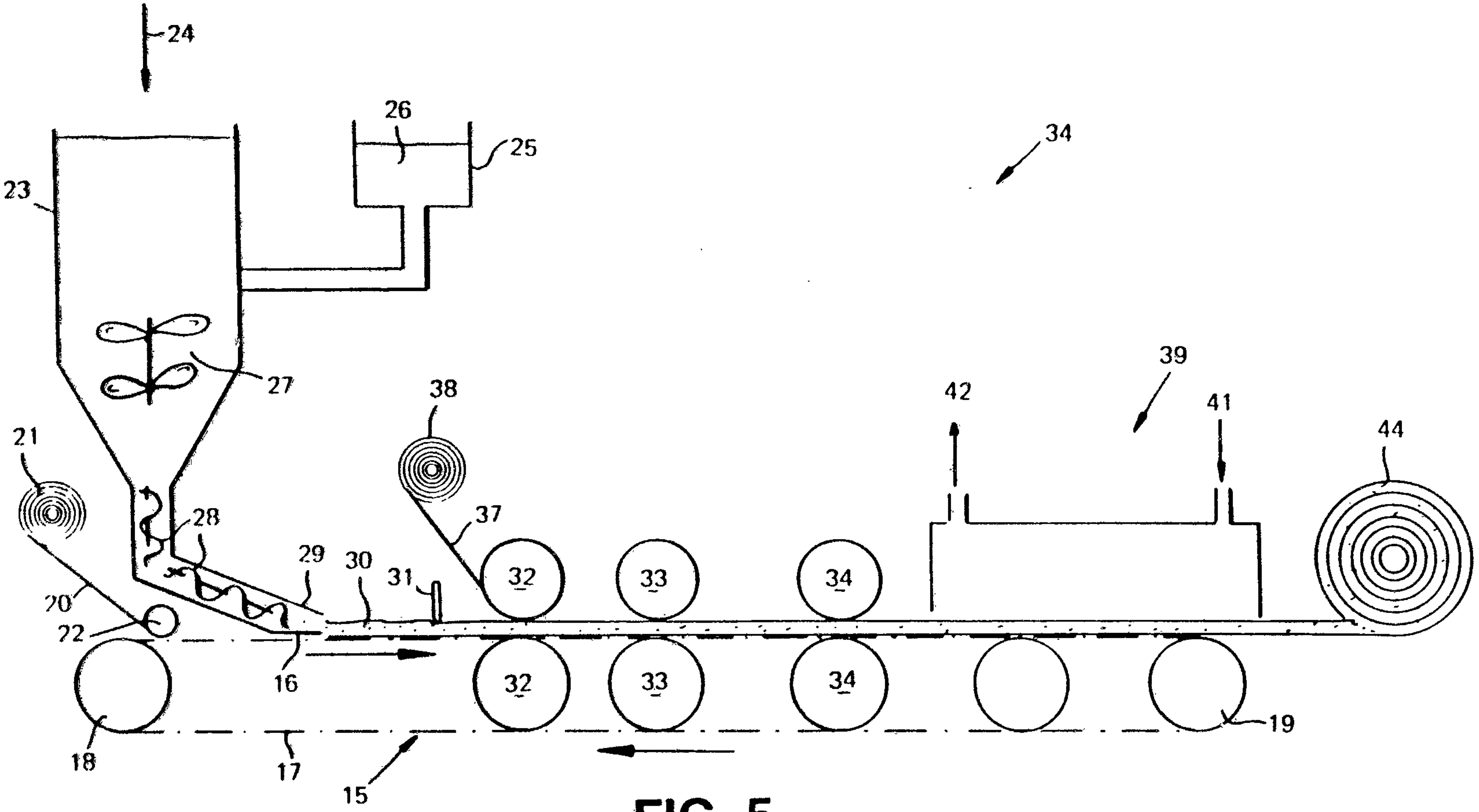
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FIG. 5

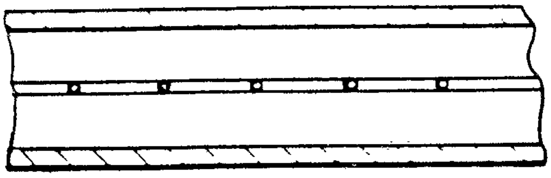


FIG. 7

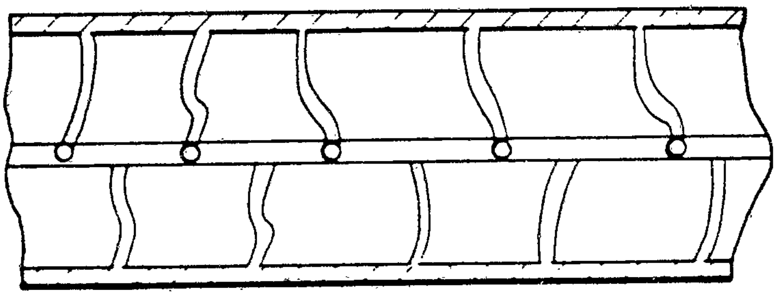


FIG. 8

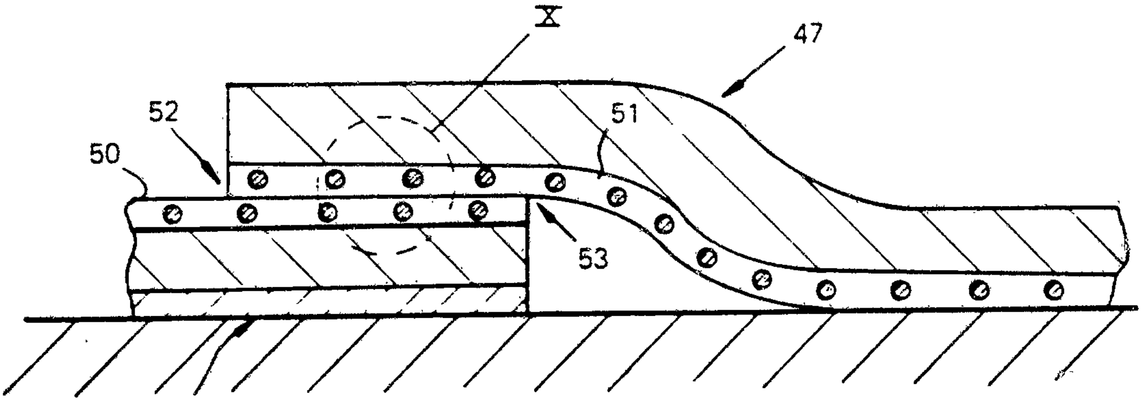


FIG. 9

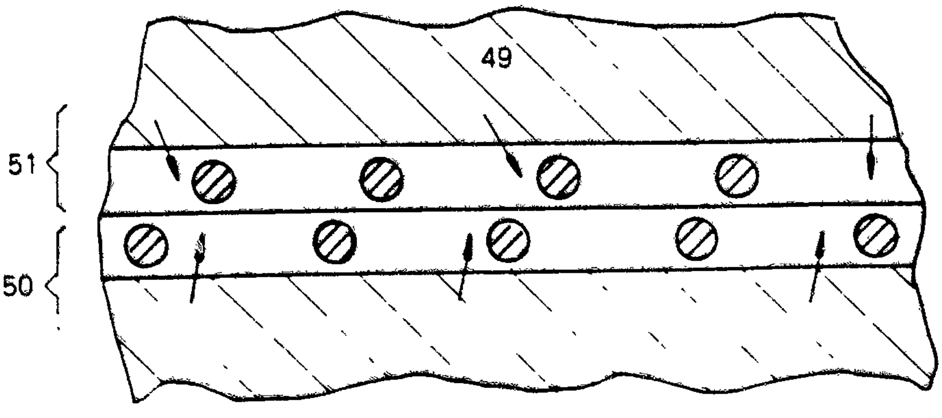


FIG. 10

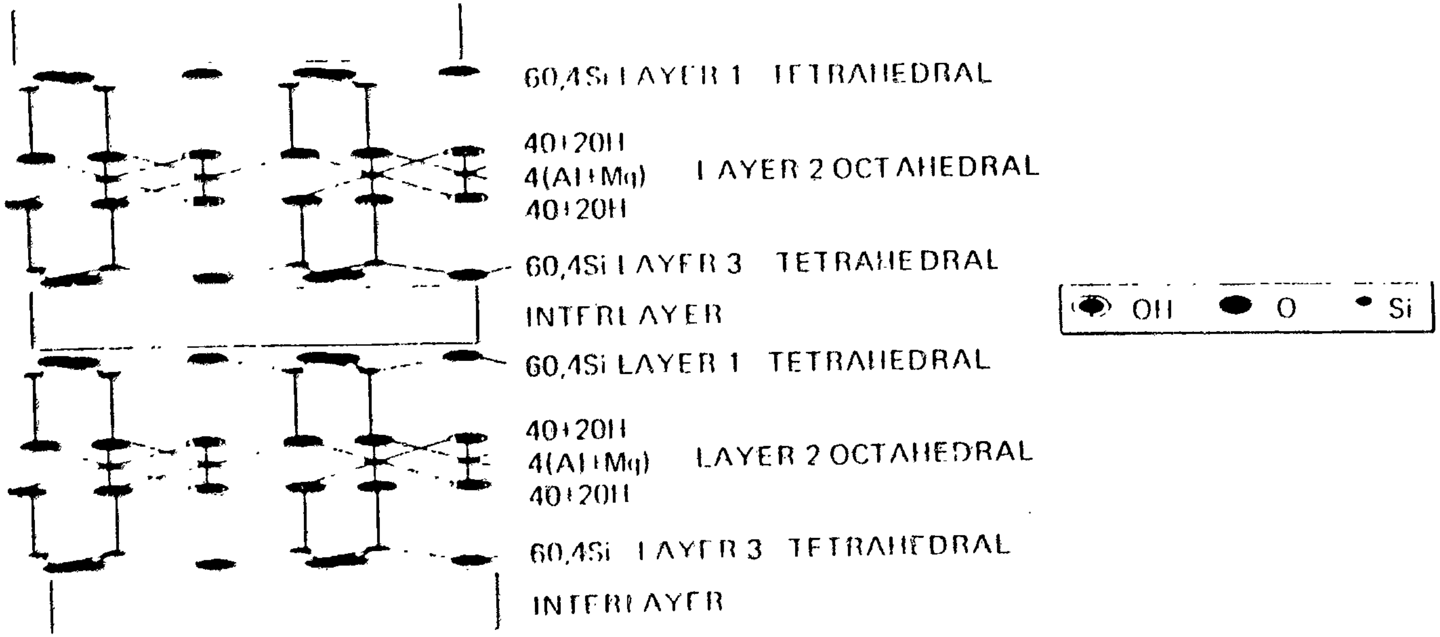
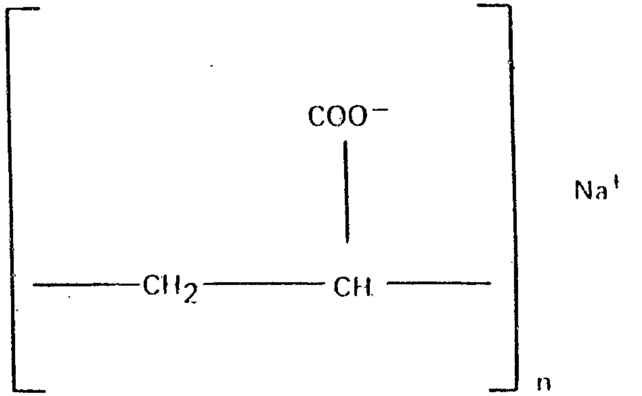


FIG. 11

FIG. 12



$$\left[-CH_2-\overset{\displaystyle COO^-}{\overset{|}{C}H}- \right]_n Na^+$$

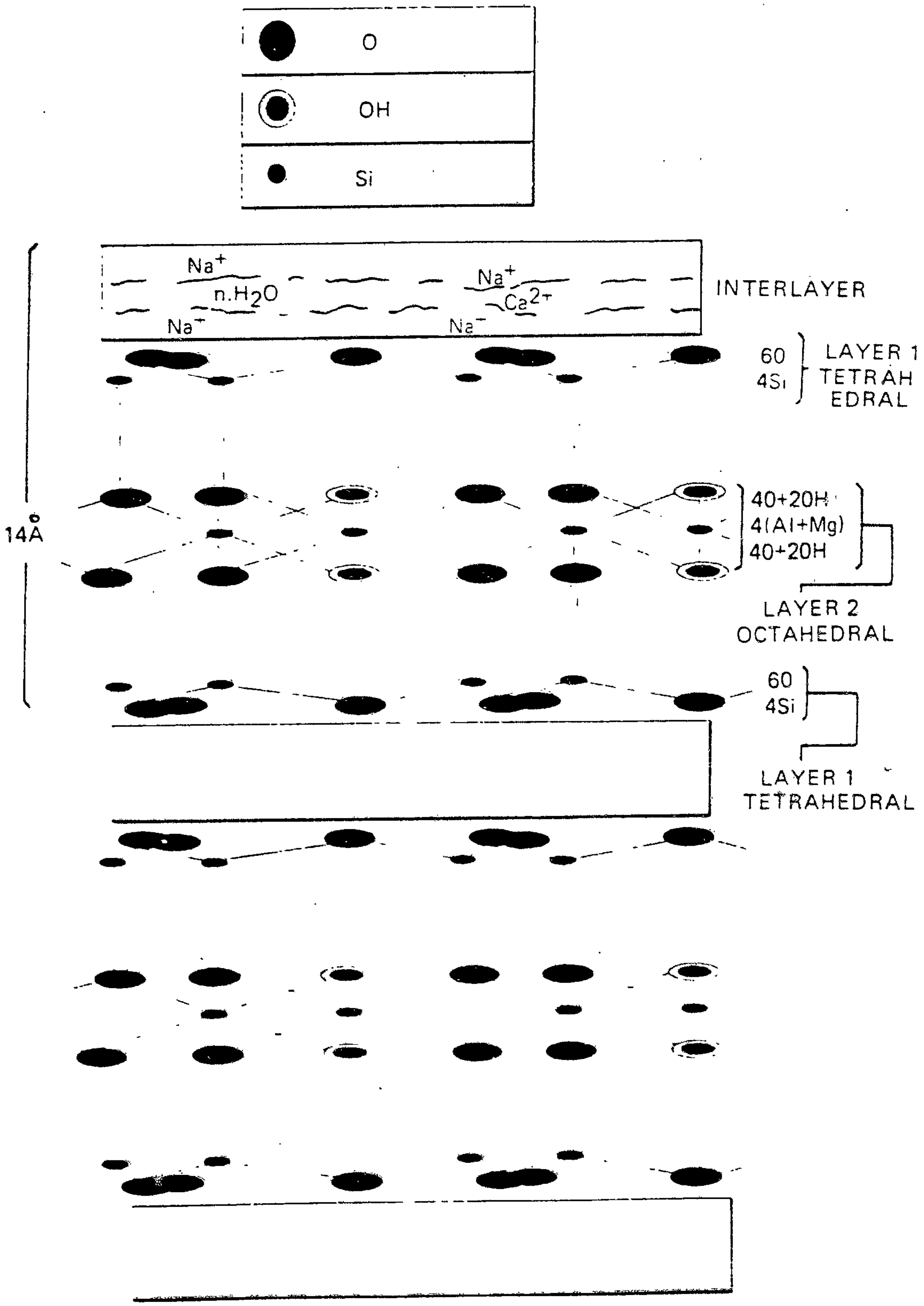

O
OH
Si
Na^+
$n.H_2O$
Na^+
Na^+
Ca^{2+}
Na^-
INTERLAYER
60
4Si
LAYER 1
TETRAH
EDRAL
14Å
40+20H
4(Al+Mg)
40+20H
LAYER 2
OCTAHEDRAL
60
4Si
LAYER 1
TETRAHEDRAL

FIG. 13

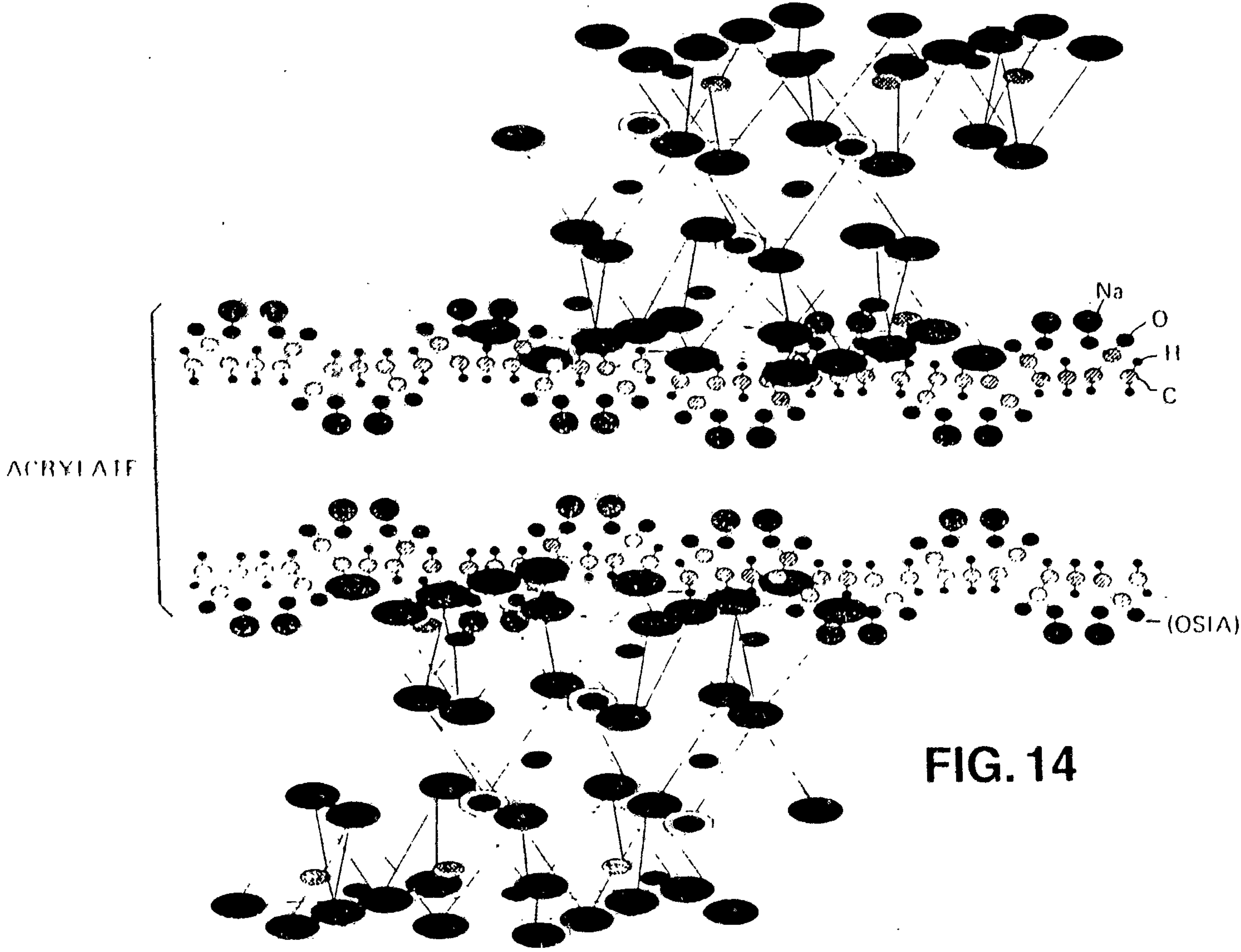


FIG. 14

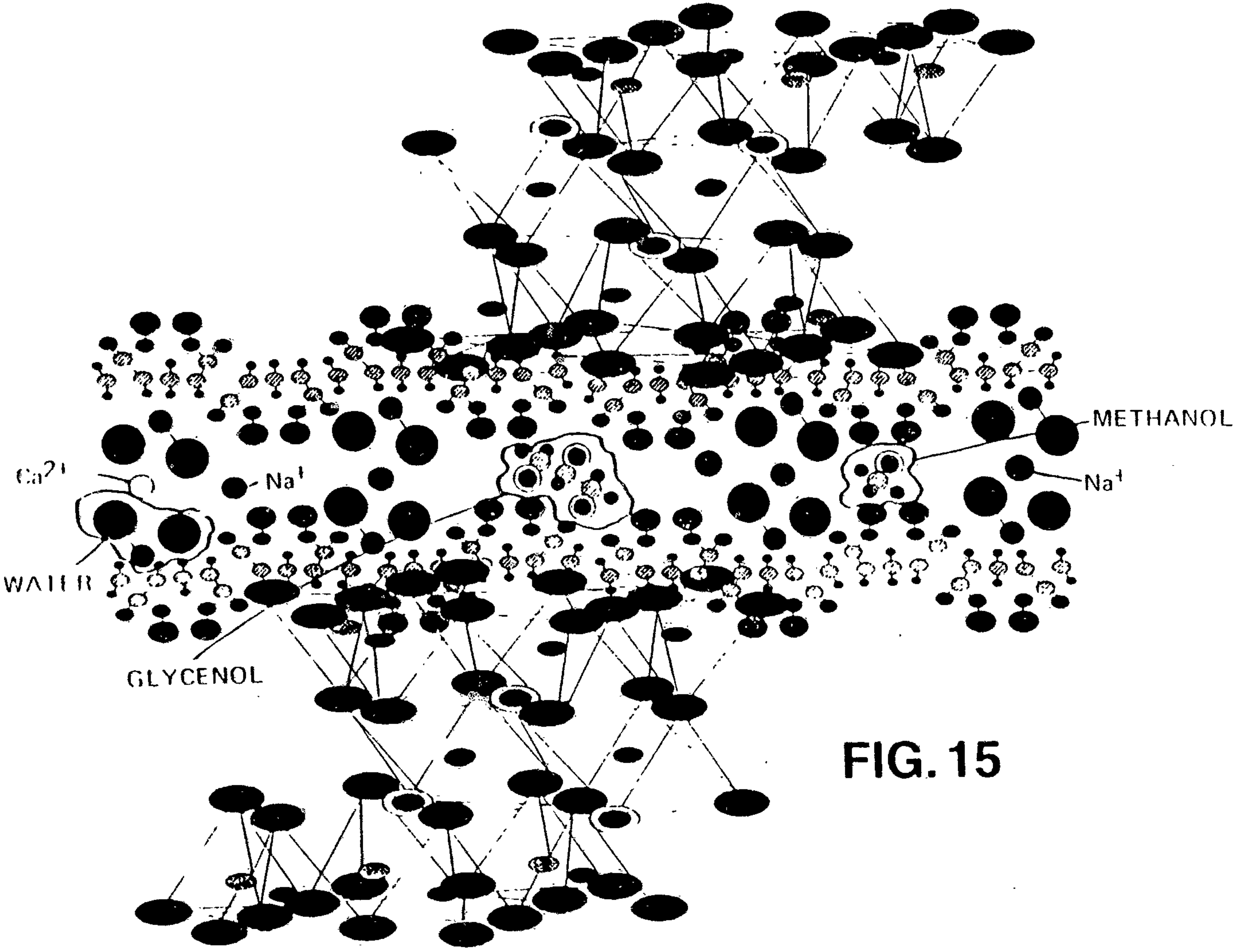


FIG. 15

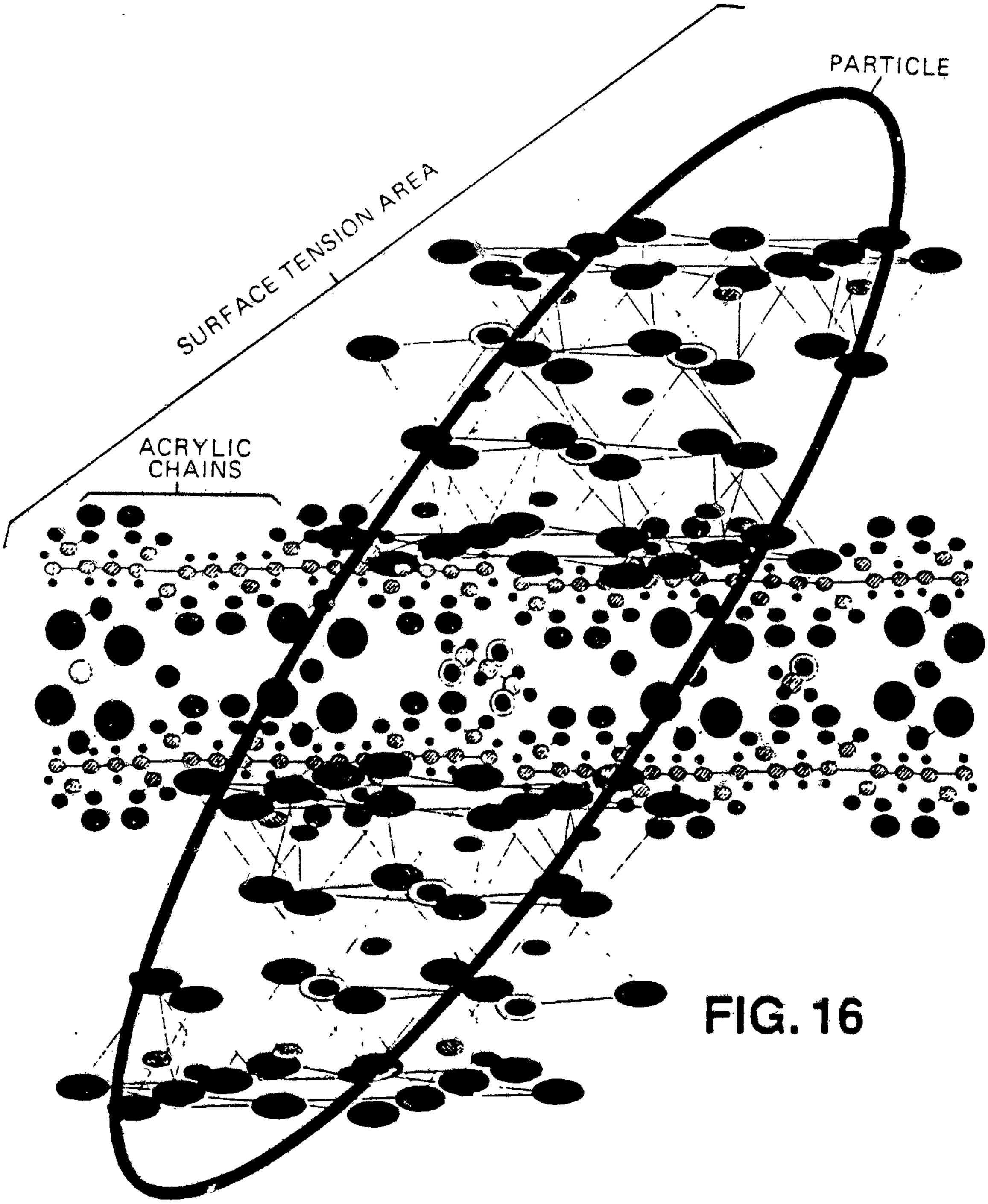


FIG. 16

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 93/01807

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 E02D31/00 B28C1/08 C01B33/34 C01B33/21 E02D19/18
E02D5/18 E02D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 E02D B28C C01B B28B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 534 925 (HARRIET) 13 August 1985 cited in the application	1,2,5, 7-10,12, 15-17, 20-22
Y	see the whole document	23
A		13,25,26

X	GB,A,2 202 185 (NAUE FASERTECHNIK GMBH & CO KG) 21 September 1988 cited in the application	1,2,5
Y	see page 1, line 1 - page 12, line 28; figures 1,2	3,4
A		10,11

X	US,A,5 091 234 (MCGROARTY) 25 February 1992	1,2,5
A	see column 2, line 13 - column 4, line 2; figures 1,2	10

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 19 July 1994	Date of mailing of the international search report 12. 08. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Tellefsen, J

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	EP,A,0 491 453 (AMERICAN COLLOID COMPANY) 24 June 1992 see column 9, line 29 - column 27, line 50; figures 1-11	1-3 5-7,10,11,15
Y A	EP,A,0 447 649 (BAYER) 25 September 1991 see column 4, line 25 - line 45; figure 1	3,4 10,11
Y	EP,A,0 059 625 (GEO-MAT INTERNATIONAL) 8 September 1982 cited in the application see page 1, line 1 - line 8 see page 5, line 8 - page 11, line 15; figures 1-5	23,27-29,32-36,38-40,43-48,50-55
Y	GB,A,2 028 710 (KARL HÄNDLE & SÖHNE) 12 March 1980 see page 2, line 36 - page 3, line 2; figures 1-6	27-29,32-36,38-40,43-48,50-55
A	US,A,2 815 292 (THIELE) 3 December 1957 see column 1, line 15 - column 2, line 26; figure 1	28,29,34-36,43,44,46-48,53,54
X	CLAY SCIENCE, vol.7, 1989, TOKYO,JP pages 243 - 251 M. OGAWA ET AL. cited in the application see abstract	64,66
X	DATABASE WPI Week 8335, Derwent Publications Ltd., London, GB; AN 83-749769 & JP,A,58 122 924 (GIKENSHA KK) 21 July 1983 see abstract	64-66

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4

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 93/01807

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 114, no. 26, 1 July 1991, Columbus, Ohio, US; abstract no. 250150d, page 170 ; see abstract & CLAY MINER., vol.26, no.1, 1991 pages 19 - 32 H. FAVRE ET AL. ---	64,65
A	CHEMICAL ABSTRACTS, vol. 113, no. 20, 12 November 1990, Columbus, Ohio, US; abstract no. 174959m, page 157 ; see abstract & FEIJINSHUKUANG, vol.1, 1990 31-2,4 M. HU ET AL. -----	64,65

4

INTERNATIONAL SEARCH REPORT

ernational application No.
PCT/GB93/01807

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.- claims 1-26: Waterproofing liner.
2.- claims 27-55: Waterproofing material
3.- claims56-92: Chemical composition of smectite clay used as a waterproofing material

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

.ormation on patent family members

Interr nal Application No
PCT/GB 93/01807

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4534925	13-08-85	US-A-	4787780	29-11-88
		US-A-	4534926	13-08-85
GB-A-2202185	21-09-88	DE-A-	3704503	25-08-88
		AU-B-	604839	03-01-91
		AU-A-	1166888	18-08-88
		DE-A-	3870273	27-05-92
		EP-A,B	0278419	17-08-88
		US-A-	5041330	20-08-91
US-A-5091234	25-02-92	NONE		
EP-A-0491453	24-06-92	US-A-	5174231	29-12-92
		US-A-	5237945	24-08-93
		AU-B-	4135093	09-09-93
		AU-B-	632684	07-01-93
		AU-A-	7599191	25-06-92
		AU-B-	640773	02-09-93
		AU-A-	7599291	25-06-92
		EP-A-	0491454	24-06-92
		JP-A-	4293825	19-10-92
		JP-A-	4247113	03-09-92
EP-A-0447649	25-09-91	DE-A-	4008791	26-09-91
		US-A-	5137393	11-08-92
EP-A-0059625	08-09-82	CA-A-	1187748	28-05-85
		US-A-	4501788	26-02-85
GB-A-2028710	12-03-80	DE-A-	2835500	14-02-80
		BE-A-	878207	03-12-79
		FR-A-	2432923	07-03-80
		NL-A-	7905865	14-02-80
US-A-2815292		NONE		