

ALIEN PROPERTY CUSTODIAN

ARTIFICIAL ASBESTOS AND PROCESS FOR MAKING SAME

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The present invention relates to a process for the manufacture of artificial asbestos-like material. It consists essentially therein that oxide-silicate foundation masses of approximately the chemical composition of the products to be manufactured but preferably containing an excess of Na_2O (if desired replaced in part by CaO) are heated in the presence of certain products, namely fluorine compounds and water, to temperatures below their melting point. Preferably the operation is carried out in a closed or indirectly heated reaction chamber.

In the case of the constituents which are not volatile under the conditions of the reaction (e. g. MgO) the differences of the composition of the starting products must not differ very much from the analytical result of the corresponding natural asbestos by e.g. 10% or even less when that particular same type of asbestos is to be obtained; if it is only desired to obtain asbestos, no matter of what composition, then it is sufficient that all the constituents of asbestos should be present in the ingredients, the combination being immaterial; Na_2O must always be present. In the case of the constituents which are volatile under the reaction conditions, in the first case if it is desired to obtain an asbestos of a certain composition such an excess must be present that quantities corresponding to those found by analysis in natural asbestos are present at the end of the reaction. In the second case if any asbestos is to be obtained it is sufficient that the constituent concerned is present at the end of the reaction, or an equivalent constituent, e.g. CaO instead of Na_2O , FeO instead of MgO , Al_2O_3 instead of SiO_2 (all may only be partly replaced). Naturally all constituents which are not absolutely necessary for the formation of asbestos can be omitted. SiO_2 , MgO , Na_2O must always be present (the last named as stated must be always present in excess compared with natural asbestos, unless another composition of the synthetic asbestos is considered), otherwise the Na_2O excess must amount from about 2% if the natural asbestos contains Na_2O to approximately 20% (with rising temperature less).

Na_2O may be replaced by CaO up to about 80%

SiO_2 may be replaced by Al_2O_3 up to about 10%

MgO may be replaced by FeO up to about 50%

The quantity of fluorine amounts approximately to 3-40% of the asbestos, the first percentage being preferably in the case of a closed reaction vessel, the latter in the case of an open reaction vessel; in the latter case 20 to 30% is the optimum quantity. The lowest quantity of water

amounts to 10% in closed reaction vessels (already introduced by the constituents of the starting mixture) to 1500%, preferably 300 to 500%. The water is preferably introduced into the reaction mixture as steam. With increasing pressure less water is necessary. The water used up by the reaction, e.g. also by escaping water-containing reaction gases is replaced in any suitable form: liquid water, steam, water-containing materials o.th.l.

When working under pressure the temperature can be as low as 250°C . and when working without pressure it can be as low as about 700° . In the former case the best results are obtained at 350° , in the latter case at about 900 to 1000° .

The minimum duration of the reaction has not definite limits, and it is possible for example to obtain a yield already after a quarter of an hour. The maximum duration depends on the reaction conditions e. g. height of the mixture of starting materials and the optimum or the practical completion of the reaction can for example be ascertained simply by the removal of samples and the quantitative analysis thereof with reference to the asbestos formed.

The same principle can be employed for the manufacture of all types of asbestos, thus therefore the non-fluorinated ingredients can be made up from oxides and SiO_2 , depending on the analysis of the natural asbestos desired which is to be manufactured. In this connection it should be noted that it is unnecessary to keep accurately within stoichiometric proportions.

The fluorine can be added to the ingredients in my desired suitable manner and that either in the cold or at higher temperatures, for example by

(a) treating them with hydrofluoric acid (gaseous or liquid);

(b) the addition of silicofluorides;

(c) passing in SiF_4 or another volatile silicon-fluorine compound; according to known reactions SiO_2 is thus added simultaneously;

(d) the introduction or passing in of any desired decomposable organic fluorine compounds;

(e) other metal fluorides, acid fluorides, double fluorides e.g. AlF_3 , NaHF_2 or cryolite;

(f) self-decomposing also non-metal fluorides, the residual portion of which does not pass into the asbestos-fibre or only in part, e.g. platinum fluoride, manganese fluoride, ammonium fluoride;

(g) the addition of elementary fluorine.

The metal oxides of the initial mixture are thus converted wholly or in part primarily before

the finishing burning into the fluorides or silico fluorides, oxyfluorides etc.

It is also possible to replace the oxides wholly or partly by equivalent quantities of other compounds, e.g. by hydroxide, carbonate, bicarbonate, chloride, oxalate, nitrate, fluoride or wholly or partly by equivalent quantities of the metals. This means that such compounds are used which under reaction condition yield the starting materials e.g. $\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O}$, $\text{NaF} \rightarrow \text{Na}_2\text{O} + \text{HF}$, $\text{MgF}_2 \rightarrow \text{MgO} + 2\text{HF}$, $\text{CaF}_2 \rightarrow \text{CaO} + 2\text{HF}$. Silicic acid can be contained in the ingredients in any desired form, that is for example as silica gel, ("active silicic acid") water-glass or kieselguhr. It is further possible to use natural minerals or rock as addition substances, e.g. magnesite, olivine, greenstone or other silicates, sand or clay, and finally artificially manufactured glasses or ceramic masses.

The formation of fibres which takes place during the burning and final ignition is helped by giving the initial mixtures a greater internal surface or providing cleft surfaces. This can be obtained by granulating the dry powdered mixture with water, better with water-glass or with salt solution, by rolling out the moistened mixture into leaflets, by the formation of plates or other kind of distortion. Further a granular formation may be obtained by the addition to the ingredients of sawdust or other combustible carrier materials or also by the addition of granulated solid water-containing silica gel which shrinks during the burning. Another method consists in embedding the components of the mixture made into a paste with water in a voluminous gel by the addition of water-glass solution, the formation of cleft surfaces taking place through the shrinking while drying or during the burning.

The mixture of ingredients thus prepared, the fluorine content of which (as fluoride and/or silico-fluoride) is preferably adjusted to 20 to 35% of its dry weight, is now subjected to ignition, preferably by indirect heating, as for example in a muffle furnace. The ignition temperature for the manufacture of all types of asbestos always lies below the melting point of the reacting mass. The temperature of ignition can be lowered if the duration is correspondingly increased. The water is already advantageously introduced as steam or superheated steam during the warming up, beginning at a temperature of the mass of 150 to 200°C. in such a way that it reaches all parts of the ingredients. The introduction of water vapour is continued with advantage through the entire ignition and after ignition. During the after-ignition at temperatures under 500° acid reagents, such as carbonic acid, hydrochloric acid or other acid vapours can be added to the steam to accelerate the removal of fluorine.

During the heating of the mixture fluorine compounds are set free as sublimates (e.g. aluminium fluoride and iron fluoride), and hydrofluoric acid and silicontetrafluoride escape. These gases or vapours can be recovered in any desired suitable manner, for example by condensation, by adsorption by means of suitable adsorbing agents, by passing into water or substances reacting with them (as for example oxides, carbonates or silicates—such as ground serpentine stone—which can combine with fluorine in this manner) and worked up for the making of a new mixture, or they can be led into the crude mixture of ingredients which still require the addition of fluorine before the final ignition, or by a combination of these regeneration methods.

The reaction atmosphere is preferably kept in a reducing state which can be effected by the addition of hydrogen or by the addition of carbon containing compounds, for example sawdust.

The mixtures may advantageously be guided through the reaction chamber on endless bands, carriages (tunnel furnace) or the like. The synthetic asbestos obtained (raw asbestos) is prepared for the various purposes for which it is required by sorting or classification according to fibre length, by treatment with acids or salt solutions (for the removal of the remaining fluorine and for permuting the bases), as well as by mechanical preparation and granulation. The removal of the fluorine is also possible by treatment with acid and water vapours. (final product).

It is sometimes advisable to ignite for a second time, the fluorine, water and Na_2O content being made up to the original quantity preferably before second ignition. Also new raw material may be added instead.

After the first ignition the fibrous material can be rendered parallel by rolling under tension.

The partial replacement of Na_2O by CaO can be carried out up to about 80%, the CaO being included in the calculation, which is sometimes already present in the natural mixture.

The so obtained intermediate and final products are new. They differ from natural asbestos in that the intermediate products (raw artificial asbestos) show a greater content in Na_2O and fluorine than the natural asbestos and a smaller room weight (weight/volume, therefore taking also in consideration the spaces between the crystals, i.e. the volume of pores) than the natural asbestos. The latter is about 0,2 to 0,6 preferably 0,3 compared with about 2,5 to 3,0 of the natural asbestos. The fluorine content of the obtained raw asbestos is about 3 to 16%, the fluorine content of the natural asbestos being up to 3%. The Na_2O content of the raw asbestos is about 3 to 15%, the Na_2O content of the natural asbestos being as a rule less than 2%. It must be mentioned that the raw asbestos obtained according to the invention is a useful and marketable product.

As to the final artificial asbestos it differs from the natural asbestos in that its room weight is about the same as of the synthetic raw asbestos.

The same applies to fluorine and Na_2O content.

The new product always contains SiO_2 , MgO and Na_2O ; a replacement may take place as lined out above on page 3.

The following examples illustrate how the invention may be carried out in practice, but it is to be understood that the invention is in no way limited to the details given in these examples.

Example 1

4 parts of magnesium oxide, 6 parts of silicic acid (e.g. as kieselguhr), 6 parts of soda, 2 parts of ammonium chloride, and 15 parts of ammonium silico-fluoride are mixed preferably under addition of 1-2 parts of saw dust and granulated with about 10 parts of a 20% waterglass solution. Thereupon the mixture is heated up to temperatures of 900-1000°C. in charges of 10 kg with the introduction of steam for 4 to 5 hours in crucibles, retorts or the like.

Example 2

10 parts of calcium carbonate, 10 parts of soda, 48 parts of silicic acid and 31 parts of magnesium fluoride are mixed (raw material) in crucibles or retorts and heated in the presence of small

quantities of steam, which is for example supplied or developed from the combustion gases of the firing or in any other desired manner until the completion of the reaction, i.e. depending on the proportions of the mixture, generally at least an hour and more up to about 1000°C. but in any case below the melting point.

Example 3

0.8 parts of fluor-spar, 1.3 parts of sodium chloride, 2.0 parts of magnesium oxide and 5.8 parts of silicic acid hydrate are mixed and heated in closed chambers, for example in retorts provided with safety valves, heatable boilers similar to those used for example for lime-sandstone manufacture, or other vessels until the completion of the formation of the asbestos in constant presence of steam to temperatures of about 1000°, but in any case below the melting point of the mixture.

According to this example the water necessary is supplied by the silicic acid hydrate. It can likewise be withdrawn from other compounds, e.g. from water-glass, hydrates or hydroxides. Further the water can be introduced as liquid or vapour into the mass in the reaction chamber before or during the reaction and preferably in small quantities, as it is used up by the reactions, adsorption, diffusion or discharge. An addition of larger quantities of water is undesirable owing to the high pressures which would then occur.

Example 4

The operation is carried out as in example 3, but the mixture contains no silicic acid hydrate. Finely ground chalcedon or kieselguhr is added to the mixture instead. In open apparatus a portion of the silicon escapes as SiF_4 , SiO_2 equivalent of which is added in excess to balance the loss. The amount of this excess depends on the size of the apparatus used and on the method of working particularly on the speed of warming up. The equilibrium $\text{SiO}_2 + 4\text{HF} \rightleftharpoons \text{SiF}_4 + 2\text{H}_2\text{O}$ is first pushed very much towards the left at about 400°C. so that at slow speeds of heating, as when using large apparatus, more SiF_4 is evolved. The optimum SiO_2 excess must therefore be determined by experiment at any time for the given conditions. For charges of 10 kg and a heating up within two hours it is about $\frac{1}{4}$ of the stoichiometrically necessary quantity of SiO_2 .

Example 5

The operation is carried out as in example 1, but an equivalent quantity of magnesite is used instead of the magnesium oxide.

Example 6

10 parts of ground serpentine are mixed with 5 parts of sodium silico-fluoride, and 3 parts of sodium chloride, and granulated with water-glass solution. (In the case of furnaces with ceramic linings hydrogen or illuminating gas is added during the reaction or the same effect is obtained more simply by the addition of carbon-containing substances, as for example about 2 parts by weight of sawdust). The mixture is heated in charges of about 10 kg for about 4 to 5 hours in retorts or crucibles or the like to 900–1000°C.

Example 7

10 parts of serpentine are melted with 14 parts of soda. The glass which contains the necessary

MgO and SiO_2 but an excess of sodium oxide is treated with a fluorine-containing mixture, for example with a mixture of 10 parts of magnesium silico-fluoride, 5 parts of magnesium chloride and 6 parts of kieselguhr which have been gelatinised with water-glass solution. The mixture is heated in charges of 10 kg for about 4 to 5 hours in retorts, crucibles or the like to 900 to 1000°C.

Example 8

The operation is carried out as in Example 7, but soda is used in part in place of the water-glass.

Example 9

100 parts of a 20% water-glass solution (from 20 parts of a Na_2O water-glass of 37° Be. and 80 parts of water) are coagulated at about 20°C. by the addition of 5 parts of magnesium silicofluoride with constant kneading. The gel which is pasty at the beginning is allowed to age (for example 24 hours at room temperature), and it is pulverised and intimately mixed (preferably by rolling) with the remaining constituents of the mixture, e.g. with a dry quantity of 12 parts of magnesium fluoride, 8 parts of SiO_2 (in the form of guhr or quartz) and 4 parts of sodium chloride. The ignition is carried out as usual. The finishing ignition temperature for this mixture lies at about 1000°.

By varying the quantity of gel, i.e. by increasing or diminishing its amount relative to the quantity of powder, it is perfectly possible to control the porous volume which is caused by the shrinking of the gel.

Example 10

5 parts of ground serpentine, 3 parts of sodium silico-fluoride and 1 part of sawdust give with 6 parts of water and 1.5 of crude hydrochloric acid a sludge which when stirred with 10 parts of a 20% water-glass solution forms a gel-like paste. After 48 hours ageing at 50 to 60°C. the finishing ignition may be carried out.

The serpentine can be replaced wholly or in part by kindred magnesium silicates, particularly by talc.

Example 11

10 parts by weight of short fibred asbestos or asbestos mixtures, obtained from the first ignition are worked up in a hollander with water to half-stuff. To this are added 2 to 4 parts by weight of sodium silico-fluoride (calculated on the quantity of asbestos) and 1 part by weight of sodium chloride (or a quantity of HCl equivalent as regards the chlorine); potato flour or dextrin is also added and to simplify the formation of the paper felt about 1 to 3% of textile waste or cellulose.

After working up on a cylinder machine to asbestos paste which is made denser by compression the recrystallising process takes place, for example in a muffle furnace by ignition at 700 to 1000°C, with the introduction of steam in a reducing atmosphere.

The product of the ignition is washed with water or more suitably boiled in autoclaves at about 150 to 200°C. with dilute acids (e.g. 1/100N HCl) or diluted magnesium chloride solution (e.g. 3%); preferably a solution of iron or aluminumchloride (5%) is used.