Nov. 12, 1940. G. W. CLARVOE ET AL 2,221,420

ARTICLE OF MANUFACTURE

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Fig. 1.

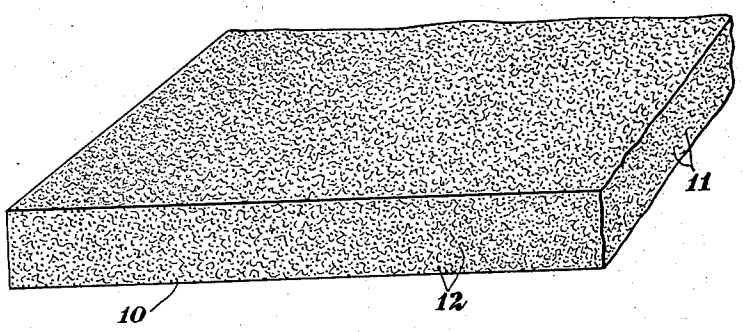
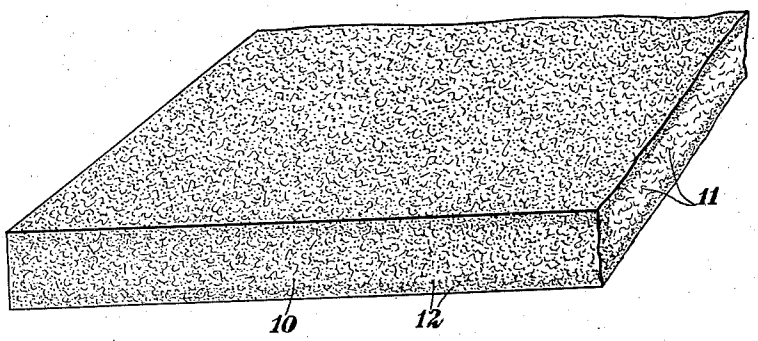


Fig. 2.



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ARTICLE OF MANUFACTURE

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Application November 18, 1937, Serial No. 175,252

9 Claims. (Cl. 260—41)

This invention relates to an article of manufacture.

More particularly, the invention relates to a sheet product, including an intimate mixture of fibres and a calcareous cementing agent, and an olefin composition of kind to be described extending throughout the outer portions at least of the article.

Sheets made in accordance with the invention are useful for structural purposes. They have advantages over impregnated asbestos-cement sheets previously known, especially for use at elevated temperatures such as would cause excessive warping of the sheets or burning out of the impregnating material in articles heretofore used at those temperatures.

The invention is illustrated in the attached drawing and will be exemplified by description in connection therewith.

Figs. 1 and 2 show perspective views, partly broken away for clearness of illustration, of portions of sheets made in accordance with the invention.

There are shown sheet products including a cementing material 10, fibres 11 distributed throughout the cement, and impregnating material 12. In the article shown in Fig. 1 the impregnating material extends throughout the entire sheet, from face to back, whereas in the article shown in Fig. 2 the material impregnates the outer portions only of the sheet. In either case, the impregnating material may extend over all edges of the sheet.

The invention will be illustrated specifically by the following detailed example.

There is first made the base sheet into which the impregnating material is later to be introduced.

In one embodiment of the invention, the base sheet is made by forming an intimate mixture of asbestos fibres, lime, finely divided silica, and water, shaping, compressing, and then hardening the compressed material.

The asbestos fibres used may be Canadian chrysotile of about the fibre length commonly used in the manufacture of asbestos-cement shingles or siding units. For best results, however, the fibres are longer and more resilient, such as well dispersed amosite fibres, either alone or mixed with chrysotile fibres. The proportion of fibres may be about 30 to 70 parts by weight to 100 parts of the total dry weight of materials in the sheet.

The silica used should be so finely ground that it reacts readily with the lime, under the influence of steam at superatmospheric pressure, as, for instance, on curing for several hours at a pressure of saturated steam of 100 to 150 pounds to the square inch. We have used to advantage comminuted diatomaceous earth of about the fineness that obtains in diatomaceous earth for use as filter aid in sugar refining.

The proportion of lime and silica may be varied somewhat, say, between 60 to 100 parts by weight or somewhat more of silica to 56 parts of lime. There is used, preferably, approximately chemically equivalent amounts of the silica and lime. In any case, there should not be used such proportions that any substantial amount of free lime will appear in the finished product, when the finished product during use is to be exposed to moisture.

The selected ingredients—fibres, lime, and silica—are mixed thoroughly with each other and with water, the proportion of water used being such as to render the mixture fluent and susceptible to ready and satisfactory shaping and consolidation.

The wet mixture is shaped into sheet form and strongly compressed, to remove some of the water. Thus, the mixture may be introduced into the bed of a hydraulic press provided with a filtering bottom and subjected there to high compression. It may be compressed, for example, at about 200 to 1,300 pounds or more to the square inch. The ram used to apply the pressure should have a face, smooth or otherwise, to impart to a face of the sheet the desired facial planeness or configuration.

The apparatus described herein is not illustrated inasmuch as it is conventional.

The thus shaped and strongly compressed, wet sheet is subjected to an elevated temperature, to cause reaction between the lime and the silica, to give calcium silicate as the heat-resistant calcareous cementing agent in the finished product. The steam-curing is effected preferably at a steam pressure of around 50 to 150 pounds to the square inch, a pressure of about 125 pounds being preferred and the steam pressure being increased very slowly to the selected maximum. The period of steaming to effect the reaction desired will vary with the temperature used and is longer the lower the maximum temperature. It is ordinarily sufficient to steam until the sheet comes to have the selected maximum temperature practically throughout and then to continue the steaming for 2 or 3 hours longer.

The steam-cured sheet is then dried until its moisture content is so low as not to interfere

with subsequent impregnation with a water-repellent fluid. Thus, the sheet may be dried at relatively low temperatures until it contains only a few per cent of water. The sheet is then more completely dried at temperatures above the boiling point of water, say to the extent produced by being maintained at about 350° F. for 1 to 2 hours, with relatively free air circulation over the sheet.

The sheet is then impregnated. The impregnating material is an olefin composition adapted to be resinified by heat, that is, to be made into a product that, after cooling, is either hard or extremely viscous. Thus, there may be used the composition separated by the fuller's earth or "clay," in the Gray tower process, from products of the cracking of petroleum. Particularly desirable is the product so separated from gasoline that has been made by cracking petroleum in the vapor phase at high temperatures of the order of 1,000 to 1,200° F. The preparation of this olefin composition is not a part of the present invention. Also, the olefin composition absorbed or separated from the gasoline fraction, in the tower process referred to, may be recovered from the tower by any usual process. Thus gasoline and other solvents in vapor phase are passed over fuller's earth, on which condensation of olefins takes place. The condensed olefins are recovered by draining from the earth suitably continuously. The tower may be warmed to an elevated temperature making the condensed olefin composition relatively mobile and adapted to flow readily from the tower. Excessive heating as well as baking at this point is avoided.

The olefin composition so recovered, in the condition in which it is marketed and initially used by us, contains a substantial amount of volatile material. Whether the "resinifying" to which we have referred is due largely or wholly to loss of volatile material or to polymerization or other chemical change that occurs on baking is immaterial to our invention. Without commitment to any theory of explanation, we include under "resinifying" all thickening and/or hardening produced by baking.

A typical olefin composition so recovered has the following features:

Content of volatile material	About 15%
Specific gravity	About 1.00 to 0.99
Iodine number (Wijs)	About 240 to 250
Molecular weight	About 415 to 435

The heat-resinifying olefin composition is impregnated into the base sheet that has been made and dried as described above. For this purpose, the said composition is first reduced in viscosity, as by being heated to 300 to 400° F. The sheet is then immersed in the warm composition and kept immersed therein until the impregnation has proceeded to the depth desired. For an impregnation of about ⅛ to $\frac{3}{32}$ of an inch, we immerse the dried sheet in the olefin composition for about 15 to 60 minutes, at 350° F.

The impregnated sheet is removed from the olefin composition, is allowed to drain for a few minutes, and is then subjected to treatment to harden or resinify the said composition. Thus, the impregnated sheet is baked for about one-half hour to 6 hours at temperatures of approximately 275 to 400° F., the duration and temperature of the baking operation depending in part upon the viscosity or hardness desired in the impregnating composition in the finished article. For most purposes, we have found satisfactory baking to the extent produced by a temperature of 300° F. maintained for about four hours.

The conditions given above are those that have been used for base sheets ⅝ to 1 inch thick. The period of time for drying, impregnation, and baking may be varied with the thickness of the sheets, being made generally longer the thicker the sheets, and vice versa.

The method described is preferably modified slightly to produce the best results. In this modification there is used an admixed agent to prevent ashing of the olefin composition, when the finished product is used at very high temperatures, as, for instance, at 450 to 500° F. For this purpose, we have found antioxidants for the olefin composition to be desirable. They are used in very small proportion, as, for example, in proportion of the order of 1% of the weight of the olefin composition, such as ½ to 2 or 3% or so. The exact amount of antioxidant to be used depends in part upon the effectiveness per unit of the agent selected and in part also upon the degree of protection required, the latter being determined by the conditions under which the finished article is to be used.

A very satisfactory agent to use with the olefin composition, for the purpose described, is phthalic anhydride. Besides decreasing the tendency to ashing, phthalic anhydride assists in the impregnation. It causes the olefin composition to penetrate more readily into the base sheet than is the case if the phthalic anhydride is omitted. Thus, the use of 1% of phthalic anhydride on the weight of the olefin practically doubles the rate of penetration of the olefin composition.

For some purposes, other antioxidants may be mixed with the olefin composition, in place of the phthalic anhydride, as, for example, phenylenediamine and gum guaiac. Hydroquinone also possesses the property of reducing to some extent the ashing of the olefin composition at elevated temperatures. However, the use of phthalic anhydride is especially advantageous.

When there is used a penetrating agent, the time required for impregnation may be shortened somewhat. Also, when an antioxidant is used, the severity of baking conditions is increased, for a given hardness desired in the baked olefin composition. Thus, the baking may be conducted for a half hour to three hours at temperatures within the range 325 to 450° F., ordinarily the time being shortened as the temperature increases, within these ranges. For instance, very desirable conditions are one hour's baking at 400° F., or two hours' at 350° F.

The resistance to ashing of products made as described may be illustrated by data for a specimen using phthalic anhydride as the antioxidant. With 1% of phthalic anhydride on the weight of the olefin composition, a sheet made as described is substantially non-ashing when maintained in contact with air at a temperature of 500° F. for 5 to 6 hours. Any ashing produced is extremely slight and is confined to a very thin superficial layer. In fact, some specimens show practically no ashing under the conditions stated.

Products made as described have other interesting properties also.

They show very little warping at moderately elevated temperatures, as, for instance, when used as a support for cores or other objects to be dried or baked in foundry practice, as described in U. S. Patent 2,035,970, issued to Mac-

Ildowie on March 31, 1936. Whereas the impregnated sheets described by MacIldowie warp badly at foundry temperatures, unless the sheets are previously repeatedly baked to establish the permanent warpage therein and then planed, as by sanding, the improved sheets made in accordance with this invention may be used directly without any such prewarping and subsequent planing. Thus, a typical sheet made by us showed a warpage of only 0.007 inch in 24 inches when baked at 300° F. for 4 hours.

Also, the product is satisfactorily resistant to abrasion, either before or after being heated to the temperature used in testing warpage.

Finally, the product is water-resistant, on the one hand, and, on the other, sufficiently porous to permit satisfactorily uniform drying of wet core plates supported thereupon and heated in the usual core drying or baking ovens, at temperatures ranging up to about 500° F.

Another type of base sheet may be substituted for the lime-silica-fibre sheet described above for impregnation by the olefin composition. Thus, there may be used a fibre-reenforced cement composition, the cement being either Portland or a cement of high calcium aluminate content (cement fondu or Lumnite cement). When Portland cement is used, there is preferably admixed with it finely divided silica in amount adequate theoretically to convert all of the basic ingredients of the Portland cement to monosilicates. In such case, the cement composition with the admixed silica is cured by steaming, say, at a pressure of saturated steam of 75 to 150 pounds to the square inch, maintained in contact with the sheet for several hours.

The fibre-reenforced cement sheet is dried and the heat-resinifying olefin composition is impregnated and baked, in the manner described above. An antioxidant is used in case the finished article is to be subjected during use to temperatures that would cause ashing in the absence of the antioxidant.

It has been found that asbestos-cement sheets made in regular manner, with plane face and without any sanding, if impregnated with the olefin composition described and then baked for several hours at about 300° F., do not warp badly during the said baking or during use as supports for foundry cores in the core drying or baking ovens.

The Portland cement, calcium aluminate cement, and calcium silicate formed by steam curing a mixture of lime and finely divided silica are examples of a calcareous cementing material.

While asbestos is preferred for the fibrous material of our improved sheets, other fibres may be used when the finished product is to be used at low or ordinary temperatures. In such a case, there may be used wood fibres, jute, hemp, or the like. Also, there may be used, besides asbestos, other mineral fibres, as for example, mineral wool, when the particularly desirable properties of asbestos are not necessary.

The details given are for the purpose of illustration, not restriction, and variations within the spirit of the invention are intended to be included in the scope of the appended claims.

What we claim is:

1. A dense, substantially non-warping, water resistant board comprising a calcareous cementing material, fibres distributed therethroughout, and a resinous polymerized olefin composition impregnated into the article.

2. A dense, substantially non-warping, water resistant board comprising a calcareous cementing material, reenforcing fibres distributed therethroughout, and a resinous polymerized olefin composition impregnating the outer portions only of the article.

3. A dense, substantially non-warping, water resistant board comprising a sheet, including fibres and a binder therefor consisting of the product of a chemically reacted mixture of lime and finely divided silica, and a resinified olefin composition in resinous condition extending throughout the outer portions of the sheet.

4. A dense, substantially non-warping, water resistant board comprising a sheet, including fibres and a binder therefor consisting of the product of a chemically reacted mixture of lime and finely divided silica, and a resinified olefin composition in resinous condition extending throughout the outer portions of the sheet, the olefin composition including an antioxidant for the said composition.

5. A dense, substantially non-warping, water resistant board comprising a sheet, including fibres and a binder therefor consisting of the product of a chemically reacted mixture of lime and finely divided silica, and a resinified olefin composition in resinous condition extending throughout the outer portions of the sheet, the said olefin composition including a small proportion of phthalic anhydride.

6. A dense, substantially non-warping, water resistant board comprising a sheet, including asbestos fibres and a binder therefor consisting of the reacted product of lime and finely divided silica, and a resinous polymerized olefin composition extending throughout the outer portions of the sheet.

7. A dense, substantially non-warping, water resistant board comprising a sheet, including an intimate mixture of asbestos fibres and Portland cement in hardened condition, and a resinous polymerized olefin composition extending throughout the outer portions of the sheet.

8. A dense, substantially non-warping, water resistant board, for use as a supporting plate for hot objects, comprising an intimate mixture of asbestos fibres and a heat-resistant calcareous cement in shaped and hardened condition and a polymerized resinous olefin composition impregnating the outer portions of the sheet.

9. A dense, substantially non-warping, water resistant board, for use as a supporting plate for hot objects, comprising an intimate mixture of asbestos fibres and a heat-resistant calcareous cement in shaped and hardened condition and a polymerized resinous olefin composition impregnating the outer portions of the sheet, the olefin composition including a very small proportion on the order of about 1% of admixed antioxidant for the said composition.

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