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# (54) Moulds.

(57) A porous ceramic mould is made by flame-spraying a layer of metal onto a replica (10) of the desired mould (19) to form a metal tool (12), filling the metal tool (12) with a freeze-gellable ceramic sol composition (17), cooling the metal tool (12) to irreversibly gel the sol composition (17) and demoulding and firing the monolith (19) so formed.

FIG. 1

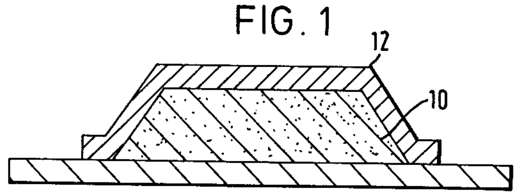



FIG. 2

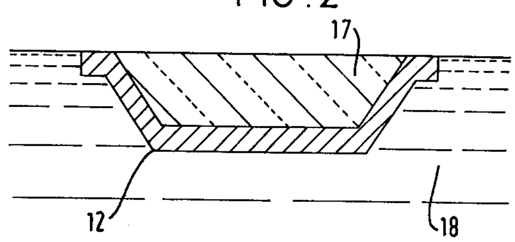
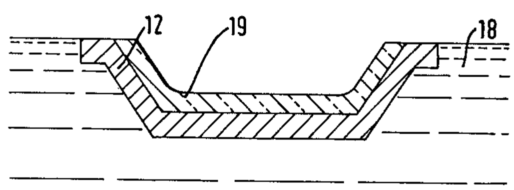



FIG. 3

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This invention relates to moulds and particularly to porous moulds as, for example, are used in the manufacture of pottery and ceramic articles by methods such as roller moulding and slip casting.

Conventionally, moulds used in slip casting and the manufacture of pottery articles are made of porous material e.g. Plaster of Paris. This material has many advantages; it is relatively inexpensive, easy to form to simple or intricate shapes and has the required degree of porosity. However, its use does entail certain disadvantages.

For example, Plaster of Paris pottery moulds are not particularly durable and, depending on the intricacy of the pattern and the quality of the product, may only last for as few as 40 moulding cycles before having to be scrapped. The material cannot be reprocessed. Another serious disadvantage is that Plaster of Paris moulds cannot withstand temperatures in excess of about 55 °C at normal humidity. Thus, drying times for the moulded product are longer than would be necessary if a higher temperature could be withstood without damage to the mould.

It will be appreciated, therefore, that despite their good qualities Plaster of Paris moulds add to the processing time and costs of the moulding operation and, because of their short life, it is necessary to carry large stocks. In the pottery industry this is a particularly serious disadvantage because of the very large number of differently shaped designs that have to be manufactured.

It has been suggested that ceramic moulds be made by immersing a suitably shaped pattern into a slurry of the ceramic composition, freeze-gelling the slurry and then firing the frozen shaped body so produced to obtain the desired mould.

While moulds produced by this means have, in principle, advantages over the above-mentioned Plaster of Paris moulds, it has not hitherto proved possible in practice to adapt this freeze-gelling technique to the reliable commercial production of a variety of mould patterns, particularly where intricate shapes are required. Although conventional metal patterns have been proposed for use in such freeze-forming processes, it has proved difficult to achieve the high degree of uniformity, particularly of thickness, that is essential to achieve uniformity of heat transference in the freezing process. This is particularly important where complex three-dimensional patterns are required.

The present invention aims to provide an improved mould which overcomes the above-mentioned disadvantages associated with Plaster of Paris and provides a ceramic mould of improved quality.

Accordingly, in one aspect the invention provides a method of making a porous mould in which a replica of the required mould is flame-sprayed with metal to form a metal tool, the metal tool is charged with a freeze-gellable ceramic sol composition, the temperature of the metal tool is lowered at a cooling rate sufficient to irreversibly gel the sol composition, the monolith so formed then being demoulded and fired.

Normally, the ceramic monolith will be allowed to thaw and dry before it is fired to give the desired ceramic mould product.

Although any ceramic sol composition may be used that can be irreversibly-gelled by freezing, the sol used is preferably a silica sol. The sol may have filler materials added to it to improve the strength of the product and to reduce shrinkage associated with drying and firing. Any suitable fillers may be used as desired. It will be appreciated that fillers should be chosen that are not chemically reactive with the freeze sensitive sol so as to avoid localised gelling without freezing.

The silica sol preferably contains from about 30% to 50% by weight, of silica, although amounts outside that range may be found to be satisfactory.

The colloidal particles in the sol are usually from 1 nanometer to 1 micron in size but preferably 2 nanometers to 100 nanometers.

The sols may be stabilised by means of sodium or ammonium ions, for example.

The replica of the desired shape may be of any suitable material, e.g. metal, wood or Plaster of Paris. Simple or very intricate shapes can be formed as the desired replica and these shapes are then accurately reproduced in metal by the spraying process. The metal tool so formed is of extremely uniform thickness and provides excellent, uniform heat-transference in the subsequent freeze-gelling process.

Moreover, the metal tool does not have the shrinkage problem associated with cast forms and so can be made to much finer tolerances.

In another aspect, the invention provides a metal pattern tool for a porous ceramic mould, the pattern tool being a flame-sprayed metal reproduction of the contours of a replica of the desired porous ceramic mould.

Because of the high degree of uniformity of the metal tools that can be made, even when of intricate design, mould products can be produced of wall thickness of greater uniformity than conventionally obtained.

The sprayed metal is preferably an alloy primarily consisting of tin and zinc but other metals and alloys, e.g. zinc, aluminium copper or brass may be used, if desired. Electric arc flame spraying is the preferred technique. Electric arc spraying is cooler than an alternative such as oxy-acetylene spraying and so there is less chance of the metal deposition damaging the replica of e.g. Plaster of Paris.

In one embodiment the finished porous mould is formed completely of the freeze-gelled ceramic sol composition, whereas, if desired, the freeze-gelled ceramic sol composition may be used as a surface coating backed with a porous and permeable base of, e.g. Plaster of Paris, to produce a composite article.

Moulds of the invention can be subjected to much higher temperature cycles in use, e.g. up to 1000 °C and so cycle times can be considerably reduced. The moulds are also stronger than corresponding Plaster of Paris moulds, they last longer and they enable stocks to be reduced.

The rate at which the ceramic sol composition is cooled is important in producing an irreversible-gelled monolithic product. The net rate of cooling will depend on various aspects of the system used. For example, the temperature may have to be as low as - 80 °C or lower to effect the desired cooling rate to the ceramic sol composition. Other temperatures may also produce the desired cooling rate dependent on the heat transfer characteristics of the system. Clearly, water-based sols may start to freeze at about 0 °C but sols based on other fluids may start to freeze at different temperatures. The skilled man of the art will readily be able to choose temperatures and cooling rates most suited to the particular circumstances.

Freezing may be achieved by any convenient means, such as, for example, pumping a cooled liquid around the metal tool containing the sol composition or placing the tool in a cooled bath e.g. of alcohol cooled with pellets of solid carbon dioxide.

The sol composition will expand on freezing and so it will be appreciated that the tool design should accommodate this expansion. For example, this can be readily achieved by leaving at least a portion of the surface area of the freezing sol composition unenclosed by the tool.

The product is thawed after removal from the tool and the water-content may then be driven off, e.g. by drying in a conventional oven or by microwave heating. The thawing and drying stages may be combined, if desired. Finally, firing at elevated temperature sufficient to consolidate the product, e.g. from 900 °C to 1200 °C, is carried out although it will be appreciated that, depending on the formulation used, temperatures well outside this range may prove suitable.

The metal tool formed by flame spraying may conveniently have a thickness of from, e.g. 0.5 to 4 mm, although for certain applications greater thicknesses may be found necessary. Clearly the thickness and the type of metal used will affect the heat transfer from the ceramic sol composition through the metal tool to the cooling liquid but the average skilled man of the art will readily be able to determine the optimum requirements for his particular circumstances and formulations.

If desired, a release coating may be applied to the metal tool or an ice-phobic coating, e.g. of a perfluoroalkoxy compound, may be applied.

Specific embodiments of the invention are now described with reference to the accompanying drawings in which:

Figure 1 is a sectional view of a first embodiment showing a sprayed metal tool on a replica mould or template of the desired shape;

Figure 2 is a sectional view showing the metal tool of Figure 1 filled with a slurry of the desired sol composition and in contact with a cooling heat transfer fluid;

Figure 3 is a sectional view of a mould of the invention formed in the tool of Figure 2;

Figure 4 is a sectional view of a second embodiment showing another freeze-gelled ceramic product formed in a metal tool; and

Figure 5 is a sectional view of another embodiment in which the tooling is designed to define both inner and outer surfaces of the mould product, a cup mould.

Referring to Figures 1 and 2, a Plaster of Paris mould 10 of the desired final shape is used as the master on which to form the metal tool 12. The mould 10 can be mounted in a suitable wooden pattern box (not shown) and its surface is varnished to seal its porosity prior to metal spraying. A water-soluble release agent, e.g. polyvinyl alcohol, is applied to the varnish-coated mould. The surface of the mould is then dried and a tin/zinc alloy is sprayed over the mould surface to a uniform depth of from 1 to 3 mm to form a metal tool 12.

The metal tool or blank 12 is soaked in water to release it from the Plaster of Paris replica 10 and its inside, i.e. moulding, surface is cleaned and then treated with a release agent. Tool 12 is then filled to the desired depth with a slurry 17 of the desired ceramic sol composition and the filled metal tool 12 is lowered into a bath of cooled heat transfer fluid 18.

When a sufficiently thick, e.g. 12 mm, layer of the ceramic sol is frozen, the remainder of the slurry is removed from of the metal tool. A shell 19 of the desired final shape is thereby obtained - see Figure 3. This is thawed, dried and fired.

It will be appreciated that, in view of the open nature of the tooling, any expansion of the sol composition during the process is automatically catered for as only the exterior surfaces of the eventual mould product are confined by the metal tool.

Figure 4 illustrates another embodiment of the invention in which a porous ceramic mould is made in a two-part metal tool using a pumped refrigerated liquid to freeze-gel the sol composition.

The metal tool is made in two parts 20 and 22. First part 20, which defines the desired product shape, i.e. the 'pattern' part, is made by flame spraying of metal on to a suitable former e.g. Plaster of Paris, (not shown). Second part 22 is shaped such that the part defined by it will fit on to a roller mould machine. Thus, part 22 may be a standard part that can be used with a variety of first or pattern parts. It can, therefore, conveniently be made by, for example, turning a metal ring in a lathe. It may also be formed hollow for the purpose described below. Tool parts 20 and 22 together define the required shape of tool cavity 23. Part 20 is sealingly attached to a backing tool 24 to define a chamber 28. The hollow portion of part 22 provides a chamber 30. Thus, 28 and 30 are chambers through which refrigerated liquid can be pumped. Inlets 32 and 34 respectively and outlets 36 and 38 respectively are provided in chambers 28 and 30 for this purpose. The mould cavity 23 is filled to the desired depth with a ceramic freeze-gellable sol composition and as the desired mould 40 starts to form, excess slurry is removed. Mould 40 is then stripped from the two-piece metal tool. It is then thawed, dried and fired.

Again, as with the previous embodiment, any expansion of the sol composition during the process is automatically catered for by the open nature of the tooling.

In Figure 5, the metal tool consists of a flame-sprayed metal shell 41 having the outline of the internal configuration of the desired cup mould 42. The external outline of cup 42 is formed by hollow aluminium back former 44 whose face 46 defines the exterior surface of the desired cup mould 42. A central hole 48 in the upper surface 50 of former 44 allows charging of the desired sol composition into the cup mould cavity defined between former 44 and metal tool 41 and also caters for any expansion of the sol composition on freezing.

Metal tool 41 is sealingly attached to a backing tool 52, which has inlet and outlet ports 54 and 56 respectively through which refrigerated liquid can be pumped. Similarly, former 44 has an inlet port 58 and outlet port 60 for the same purpose. It is also provided with a drain outlet 62.

After freezing the sol composition the cup mould 42 is stripped from the tooling, thawed, dried and fired.

## Claims

1. A method of making a porous mould in which a tool of the desired shape is charged with a freeze-gellable ceramic sol composition and the composition is frozen, characterised in that a replica (10) of the desired porous mould is flame-sprayed with metal to form a metal tool (12), the metal tool is charged with the freeze-gellable composition (17), the temperature of the metal tool is lowered at a cooling rate sufficient to irreversibly gel the sol composition, the monolith (19) so formed then being demoulded and fired.

2. A method according to Claim 1, characterised in that the monolith (19) is allowed to thaw prior to firing.

3. A method according to Claim 1 or 2, characterised in that the ceramic sol composition (17) is a silica sol.

4. A method according to Claim 3, characterised in that the silica sol contains from 30 to 50% by weight of silica.

5. A method according to any one of the preceding claims, characterised in that the sol composition is stabilised with sodium or ammonium ions.

6. A method according to any one of the preceding claims, characterised in that the flame spraying is electric arc spraying or oxy acetylene flame-spraying.

7. A method according to any one of the preceding claims, characterised in that the sprayed metal is an alloy of tin and zinc or is of zinc, aluminium, copper or brass.

8. A method according to any one of the preceding claims, characterised in that the temperature of the metal tool (12) is lowered by passing a cooled liquid (18) into contact with it.

9. A method according to Claim 8, characterised in that the metal tool (20, 22) is hollow and the cooled liquid is passed through it.

10. A method according to any one of the preceding claims, characterised in that the porous mould is formed as a composite in which the monolith formed from the freeze-gelled composition provides the mould surface and is attached to a different permeable backing layer.

11. A metal pattern tool for a porous, ceramic mould, characterised in that the pattern tool is a flame-sprayed metal reproduction of a replica (10) of the desired porous ceramic mould (19).

**12.** A metal pattern tool according to Claim 11, characterised in that the metal is an alloy of tin and zinc.

**13.** A metal pattern tool according to Claim 11, characterised in that the metal is zinc, aluminium, copper or brass.

**14.** A metal pattern tool according to Claim 11, 12 or 13, characterised in that it is hollow and adapted to receive cooling liquid.

**15.** A metal pattern tool according to any one of Claims 11 to 14, characterised in that it has a thickness of from 0.5 to 4 mm.

FIG. 1

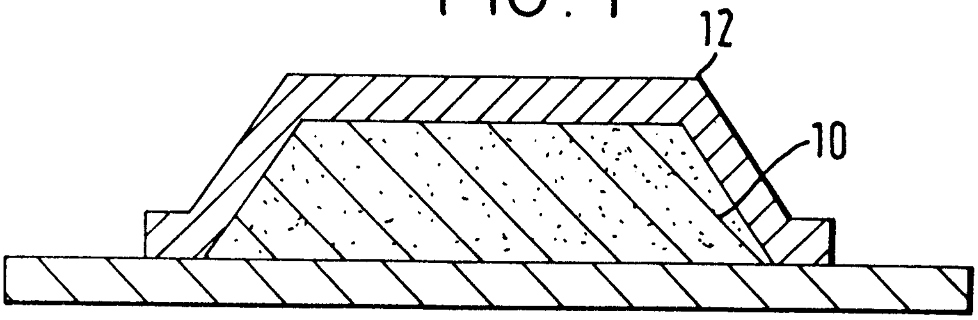


FIG. 2

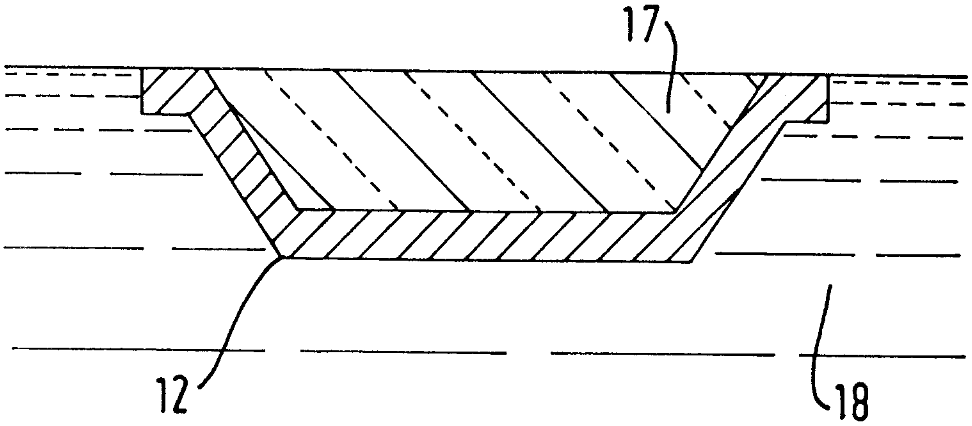


FIG. 3

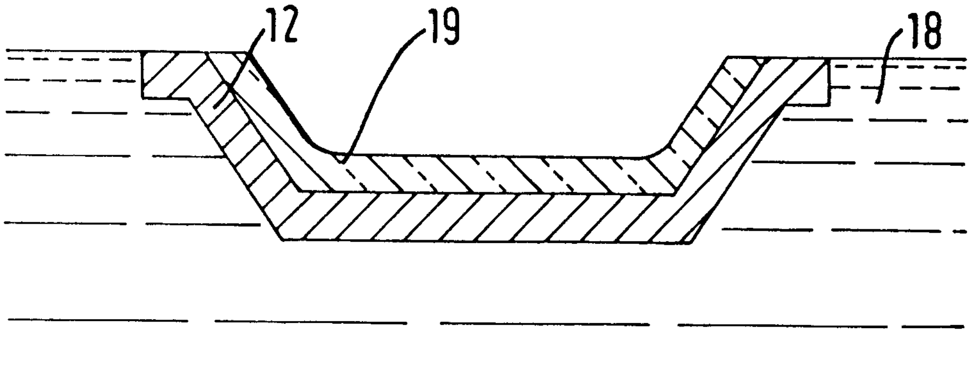

FIG. 4

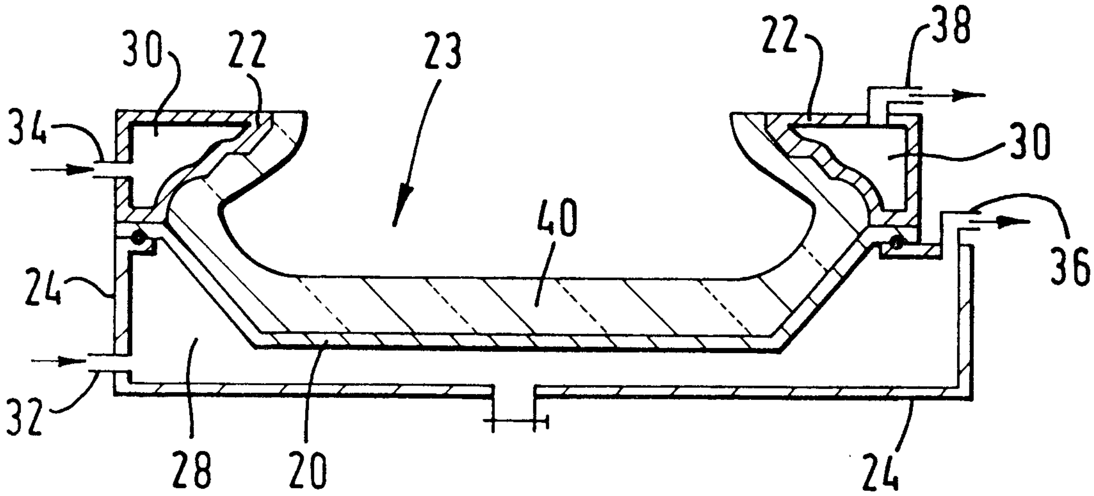
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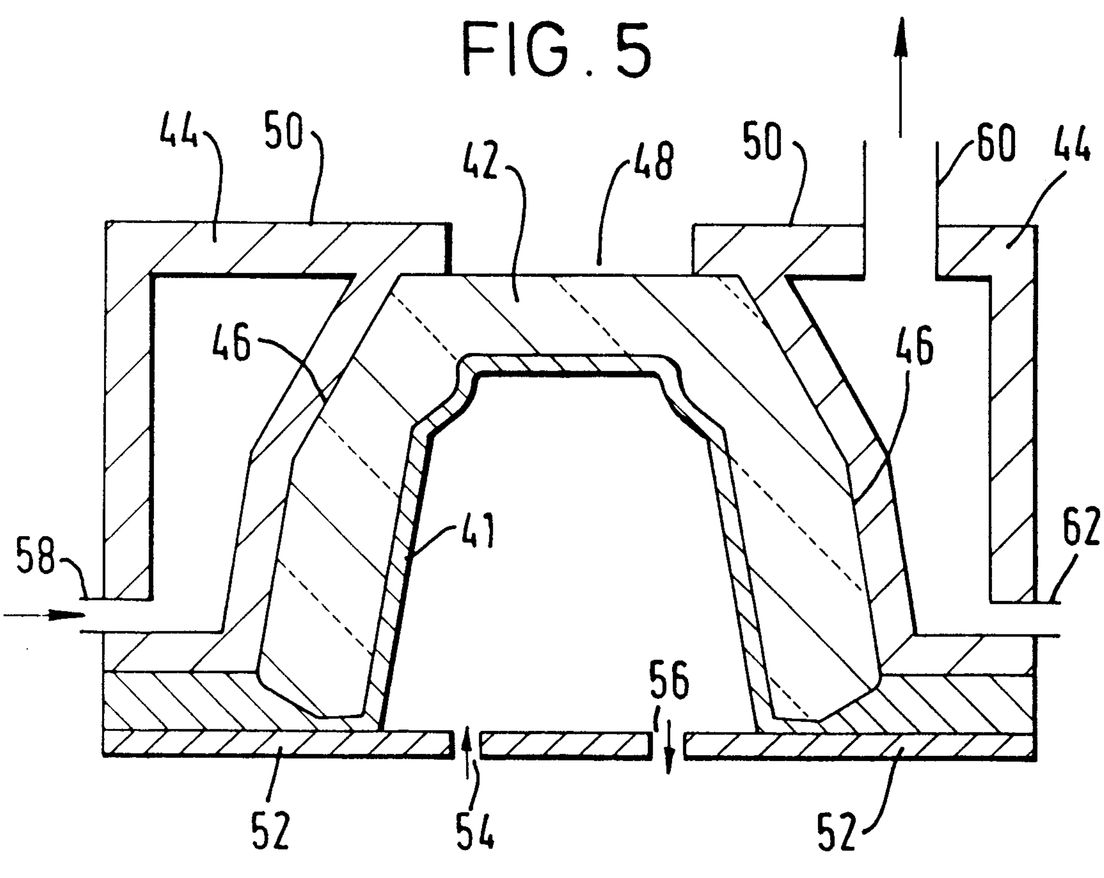
FIG. 5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# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 8671

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5 ) |
|---|---|---|---|
| A | GB-A-1 175 838 (NORTON ABRASIVES LIMITED) * the whole document * --- | 1,11 | B28B7/34 B28B1/26 B28B1/00 B29C33/38 |
| X | WO-A-8 302 251 (DRABERT SÖHNE) * the whole document * --- | 11-13 | |
| A | GB-A-616 172 (E.J. JOHNSON) * figures * --- | 1,11 | |
| A | US-A-3 816 572 (H.M. ROELOFS) * claims * --- | 1-4,8 | |
| A | US-A-4 231 982 (JANSSON) * the whole document * ----- | 1,11 | |

TECHNICAL FIELDS SEARCHED (Int. Cl.5 )

B28B
B29C

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 08 JANUARY 1993 | LASSON C.Y.M. |

CATEGORY OF CITED DOCUMENTS

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