March 9, 1943. R. NEIMAN ET AL 2,313,085

INVESTMENT COMPOSITION

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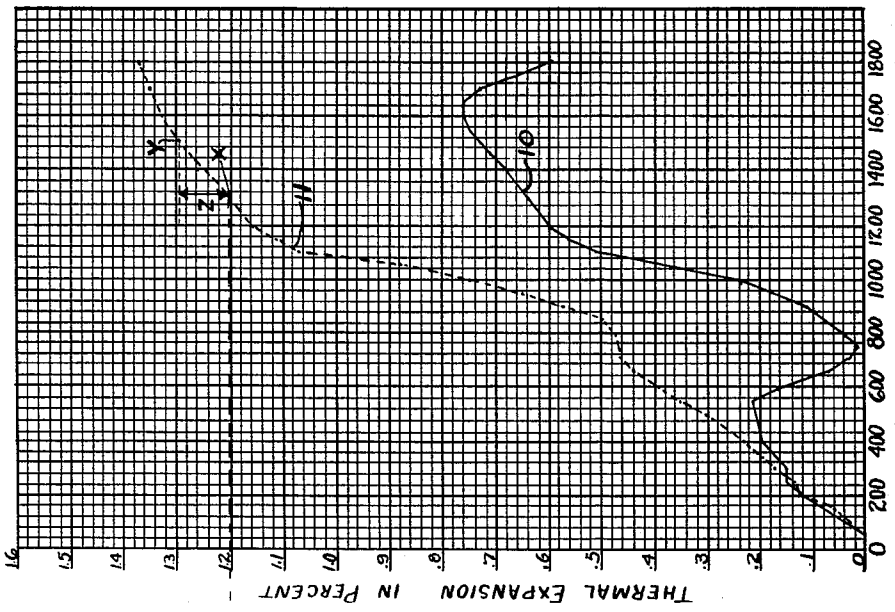


Fig. 1.

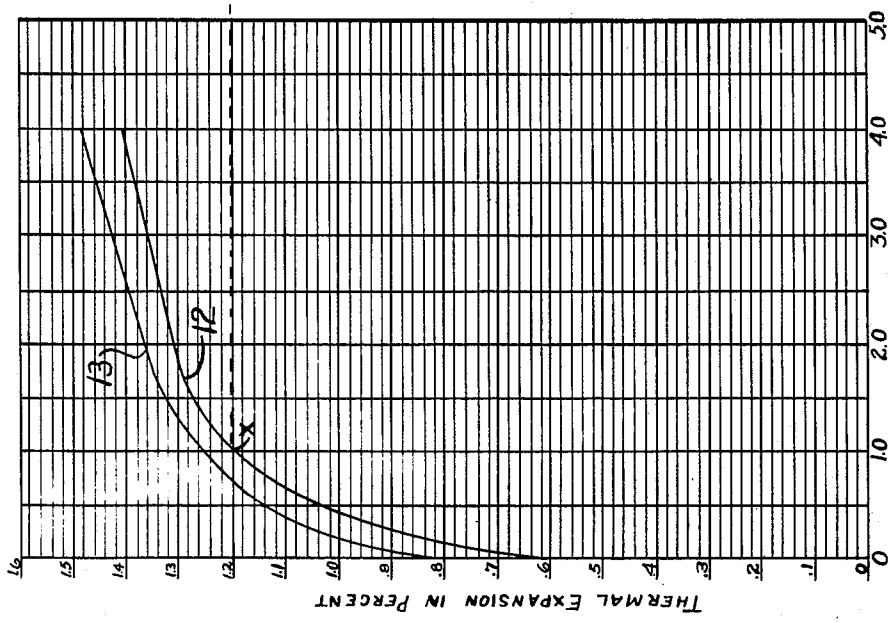


Fig. 2.

INVENTORS.
ROBERT NEIMAN
ROBERT C. ERNST
EDMUND A. STEINBOCK

BY Joseph A. Rave
ATTORNEY.

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INVESTMENT COMPOSITION

Robert Neiman, Robert C. Ernst and Edmund A. Steinbock, Louisville, Ky.; said Neiman and said Ernst assignors to University of Louisville, Louisville, Ky., a corporation of Kentucky

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12 Claims. (Cl. 22—188)

This invention relates to investment compositions for making refractory molds into which metals, such as precious metals or othe suitable casting material can be cast into objects which must conform with great exactness to a predetermined size and shape.

This invention will be described in its application to making dental castings such as inlays, which castings must be very accurately made as far as size and shape are concerned, but it is to be understood that the composition has general application in industry generally.

In making dental inlays or inlay restorations, wax models of the exact size and shape of the cavity to be filled are first made and then invested in a composition generally known as investment compositions, that is, a plastic mass which sets to a hard refractory mold. After the investment sets, the mold is heated to a temperature of 800° F. to 1800° F., in order to melt and burn out the wax, and also to prepare the mold for casting. Any suitable or desirable method may then be employed in casting. Usually, use is made of some machine which forces the molten metal, under pressure, into the cavity formerly occupied by the wax. The mold is then cooled by plunging it into water, and is then broken apart to obtain the casting. The casting is then cleaned and polished for use. Obviously, if the mold used had expanded sufficiently, prior to the casting process, to counteract exactly the casting shrinkage of the metal or alloy, the finished casting will require but little attention in fitting it into the accurately, previously prepared cavity.

In order to make the casting conform to a predetermined size and shape, that is, to the original pattern, it is important that the mold be expanded sufficiently first, prior to the casting operation, to counteract the shrinkage in the metal or alloy that takes place when the metal cools and solidifies during this casting process. This shrinkage to be counteracted varies from .9% to over 2.%, depending on the size and shape of the casting and type of casting alloy used. For dental inlays, it varies from approximately .9% to 1.4%.

The investments now commercially available, and termed simple investment compositions, consist principally of a binder, a refractory filler, and one or more modifying agents. The binder generally consists of plaster of Paris. There are several forms of calcium sulfate that may be used and which will act similar to plaster of Paris. Plaster of Paris is known as hemihydrate ($CaSO_4.\frac{1}{2}H_2O$) and generally has a testing consistency of 60 parts of water to 100 parts of plaster. Another form of hemihydrate, known as alpha gypsum, and commercially known as "Hydrocal," generally has a testing consistency of approximately 40 parts of water to 100 parts of alpha gypsum. This lower consistency is advantageous in increasing the expansion and also the strength of the mold. There are several other forms of calcium sulfate, both hydrated and dehydrated, that set when gaged with water, and may also act as a binder. The term binder will be used hereinafter to cover any, or a mixture, of the above forms. All test results and curves, wherein the term plaster is referred to hereinafter, were made with the alpha gypsum or "Hydrocal" form, which, as mentioned above, is the preferred form.

The refractory filler as generally used consists principally of siliceous matter. Since the chief property desired, and the one most difficult of attainment, in an investment composition is a high thermal expansion, it is obvious that refractory fillers with inherent high expansions are to be preferred. Silica, in its three principal modifications, quartz, tridymite and cristobalite, possesses high expansions along with good refractory properties and in addition is fairly inexpensive. The quartz form is least expensive and almost always used. Hereinafter, the term silica may be construed as meaning quartz. Of the three forms, cristobalite has the greatest expansion and when used to replace all or part of the quartz form, will impart a greater expansion to the mold in proportion to the amount used.

Many other types of refractory materials may be used to replace all or part of the silica and include such refractory materials as magnesia, alumina, chromium oxide, refractory clays and many silicates. A number of silicates, and in fact several oxides, alone have unusually high expansions due to change of phase or inversion. Wherever these materials have melting points sufficiently high to permit successful use in investments they may be used advantageously as part or all of the refractory filler.

The term refractory filler, when used hereinafter, shall be construed to include any of the above mentioned refractories, alone or in any mixture thereof, or any material having substantially the same property of withstanding the temperatures encountered in the casting process, and which are compatible with the other ingredients.

In addition to the binder and refractory filler,

it is desirable to add one or more of the following agents to adjust the setting or hardening characteristics, improve the smoothness or porosity of the mold, or otherwise impart desirable physical or chemical action to the mold surface so as to produce the smoothest, densest and least contaminated casting possible. Such materials include accelerators, retarders, reducing agents (such as graphite), fine clay, powdered metals and oxides as well as agents to reduce the amount of gaging water necessary.

The above simple type of investment composition does not have the desired thermal expansion in conjunction with proper strength, nor several other desirable characteristics. For example, a mixture of 44 parts plaster and 56 parts silica, and gaged with 26 parts of water, will show an expansion of but .64% at 1300° F. Several materials have been found that will increase the thermal expansion of such a mixture when used in replacing part of the silica. Some of these materials include boric acid, cristobalite and chlorides, such as sodium, potassium and lithium. Each of these has a particular value in increasing the expansion within limited temperature ranges, but generally effect a shrinkage in the molds at the higher temperatures, especially 1600 to 1800° F.

It is therefore the principal object of this invention to provide an investment composition for use in casting, principally, by the disappearing wax pattern method that will withstand high temperatures of heat and give the desired or necessary amount of thermal expansion at these high temperatures.

It is also an object of this invention to provide an investment composition for making molds that is considerably stronger than those heretofore used at temperatures where at least equal expansion is obtained.

It is a further object of this invention to provide an investment composition having a greater thermal expansion than those previously known and used without employing a greater amount of thermal expansion improving agent.

It is a still further object of this invention to provide an investment composition in which the setting expansion and setting time can be controlled or modified by the thermal expansion improving agent itself.

Other objects and advantages of this invention can be readily apparent by reference to the following specification, considered in conjunction with the accompanying drawing forming a part thereof, and it is understood that any modifications can be made within the scope of the appended claims, without departing from or exceeding the spirit of the invention.

In the drawing:

Fig. 1 shows a pair of graphs illustrating the expansion of two investment compositions when heated under identical conditions.

Fig. 2 shows a pair of graphs of investment compositions illustrating the expansion when heated to a single given temperature with different amounts of the thermal expanding improving agent each with the same base respectively.

As was noted above, investment compositions for dental and other purposes have been known and used for many years. This general or simple composition has comprised from 18 to 50 percent plaster and from 82 to 50% silica. The thermal expansions of such compositions increase with an increase in the silica content, but the strength of the resulting mold correspondingly decreases. The proportions of these ingredients as just set forth may be varied beyond these limits, depending upon the exact technique used in producing castings.

In Fig. 1 of the drawing, the reference numeral 10 indicates the thermal expansion and contraction of a mixture of 44% plaster and 56% silica, and indicates a thermal expansion of .64% between room temperature and 1300° F. This investment was made with a water to powder ratio (W/P) of .26, that is, 26 parts of water to 100 parts of the powder mixture on a weight basis. An increase of the W/P causes a material decrease in the thermal expansion of this type of mixture. It should be noted however that while the converse is true, the W/P above set forth is, from a commercial standpoint, about as low as practicable.

In Fig. 1 of the drawing, the curve indicated by the reference numeral 11 shows the thermal expansion resulting from a modification of the simple investment composition by adding to said simple investment composition one part by weight of potassium bromide for an equal amount of silica. In this composition, the W/P ratio was held as above, that is, .26. As will be seen, this resulted in a thermal expansion of 1.20% between room temperature and 1300° F.

By comparison of the curves 10 and 11, it will be noted that the 1% of potassium bromide produced an investment composition that was, throughout the heating period, expanding regularly while the other or simple investment composition expanded, contracted and then reexpanded. In commercial practice, especially on comparatively large molds, there is often a temperature differential of several hundred degrees between different parts of the mold. Obviously, if one part is expanding and another contracting, distortion and cracking often takes place. In the modified composition, such danger is practically eliminated. It should be noted at this point that gold alloys are generally cast around 1300° F., and at this casting temperature have a casting shrinkage of 1.25%. The potassium bromide composition at this casting temperature has very nearly this thermal expansion, namely, 1.20%, whereas the simple investment composition has practically one half of the necessary thermal expansion. This difference in casting shrinkage and mold thermal expansion, or .05%, may be made up by modifying agents in the composition, but preferably by the addition of a fractional part of the potassium bromide, such as an additional .3% or part, or a total of 1.3% of the potassium bromide. Ofter this is not necessary as the setting expansion may more than counteract the wax pattern shrinkage, and thus a thermal expansion of 1.25% is not always necessary, but generally desirable.

As was noted above, other thermal expanding improving agents have been employed, such for example as sodium chloride and boric acid. It should be noted that one percent of sodium chloride in place of the one percent potassium bromide would give only 1.00% expansion, while one percent of boric acid would only give approximately .9% thermal expansion.

In Fig. 2, the curve indicated by the reference character 12, shows the thermal expansion of a simple composition when augmented with different amounts of the thermal expanding improving agent potassium bromide as mentioned above. In other words, 2% or parts of potassium

bromide for an equal amount of silica increases the thermal expansion at 1300° F. to 1.31%; 3% or parts of potassium bromide for a similar amount of silica raised the thermal expansion to 1.37%, while 4% or parts of potassium bromide raised the thermal expansion to 1.40%. From the foregoing, it will be noted that the more potassium bromide employed, the greater the thermal expansion at a given temperature. It will also be noted that the amount of increased thermal expansion does not proportionately increase in accordance with the increased amount of potassium bromide used, and that a limit will be reached beyond which no further increase in thermal expansion will take place. This maximum amount being approximately 5 to 8% or parts of the total solid ingredients of the investment. The greatest thermal expansion increase being obtained with the first unit of potassium bromide added to the composition, and that subsequent units of potassium bromide have a constantly decreasing increasing effect on the thermal expansion. From the foregoing it will also be noted that should less thermal expansion be desired, such as is obtained with sodium chloride or boric acid, considerably less than 1% of potassium bromide may be employed, or with an equal amount of expanding agent, more binder may be added with subsequent increase in mold strength.

As was noted above, with an increase in the silica content in the simple investment composition, (with a consequent decrease in plaster) the thermal expansion can be increased, and this thermal expansion can be further increased by the substitution of small amounts of potassium bromide for corresponding amounts of the silica. The curve in Fig. 2, indicated by the reference character **13**, is an example of such a composition, namely, a composition which includes 30% plaster, 0 to 4% potassium bromide and the balance silica. By comparing curves **11** and **12**, it will be noted that the decrease in plaster (increase in silica) has resulted in a curve having approximately .1% more thermal expansion throughout the range illustrated. It should be noted further that these curves, indicated by reference characters **12** and **13**, are summary plots of the 1300° F. points on the thermal expansion curves in which varying amounts of potassium bromide were added to simple investment base compositions. The small letter *x* found in Figs. 1 and 2 and on curves denoted by reference numerals **11** and **12** and connected with a dash line are the same points. It may also be noted that if the summary plots were made for any other temperature, the shape of the curves in Fig. 2 would be the same except that the vertical intercepts would be raised or lowered in the same amount shown on the curve denoted by reference numeral **11** in Fig. 1. For example, if the temperature chosen is 1500° F., the whole curves in Fig. 2 would be raised by the amount shown by the vertical distance between point *x* and *y* in curve **11** on Fig. 1, namely, *z* (.14%). Likewise, a summary plot at a lower temperature would correspond, but at a lower point in vertical heighth.

Whereas in the above simple investment composition the increase in W/P causes a decrease in the expansion, the same is true with compositions containing the addition of potassium bromide, but not to such marked degree. Obviously, this is advantageous where care is not taken to adjust the W/P ratio accurately. It is also to be noted that, since the decrease in W/P increases the strength of the mold, the addition of any material which will not affect the thermal expansion or other casting characteristics of the investment composition and still enable a further decrease in W/P or impart to the composition a greater plasticity at the same W/P will be of added advantage.

The foregoing description deals specifically with potassium bromide as the thermal expansion improving agent; it has been found however that substantially all the other soluble inorganic bromides have a similar thermal expansion improving agent effect. Potassium bromide being a widely used commercial chemical is relatively expensive and the least deliquescent of the bromides, and therefore most suitable for these reasons. Where it is advisable to produce a mold wherein the cation potassium may not be compatible with the other ingredients, or where some of the other bromides, perhaps available commercially in a more impure form, and consequently less costly, or offering other advantages, substantially equal increase in thermal expansion will be produced by the following bromides, namely, those of ammonium, potassium, sodium, lithium, rubidium, caesium, barium, calcium, strontium and magnesium. The thermal expansion is increased to a somewhat lesser degree by the bromides of the following cations or metals, namely, iron, zinc, nickel, cobalt, chromium, manganese and aluminum. Somewhat less desirable, but still able to produce considerable increase in expansion are the following bromides, namely, cadmium, copper, lead, bismuth, antimony and tin. Hydrogen bromide or hydrobromic acid will also produce considerable benefit in expansion increase. Should this acid be used, gas bubbles will usually be formed by reaction with impurities in the plaster but may be removed by vigorous mixing. Other soluble inorganic bromides were not commercially available at the time tests were made; however, it would be fairly safe to predict that their action would be similar to those mentioned above.

While the bromides are generally decomposed at high temperatures, this does not appreciably affect the expansion properties of the composition. For example ammonium bromide is more than likely entirely eliminated at the usual casting temperatures but nevertheless it has imparted some action, at present not explainable scientifically, to the mold, which enables expansions to continue even though the added agent is no longer present. The bromides are also generally beneficial as cleansing agents in improving the surface appearance of the casting. Some of the bromides may form oxides when heated, but nevertheless their beneficial expansion increasing and cleansing properties are not imparted to the mold if the respective oxide were originally added in place of the bromide.

From most standpoints, including beneficial effects on setting and thermal expansions, as well as action as accelerators, the above bromides act substantially the same as the potassium bromide which was used throughout as an example. It is to be noted however that while the amounts used may have some benefit slightly above 5%, the cost involved and the fact that they are somewhat less desirable from a moisture absorbing standpoint, it would be desirable to use perhaps not over 3% of these.

In general commercial practice, the various bromides would be added and mixed with the plaster and silica powders but where the moisture absorbing characteristics are undesirable the same

beneficial results may be secured by adding the bromide to the gaging water instead.

As mentioned above, when describing the refractory filler in an investment composition, materials other than quartz may be substituted for all or part of the latter. Perhaps the most suitable refractory now available which will impart greater expansion to the mold than its equivalent amount of quartz is cristobalite. Using 44% plaster with 1% potassium bromide, and with 55% silica the thermal expansion at 1300° F. will be 1.20%. By substituting cristobalite for all of the quartz in the above investment composition, the thermal expansion will be raised to approximately 1.6 to 1.9%, depending upon the type and purity of the cristobalite. Where only a portion of the quartz is replaced by an equal amount of cristobalite, the expansion will be increased in proportion to the amount of cristobalite used. Thus, using 44% plaster and 1% potassium bromide, and with varying amounts of quartz and cristobalite, any thermal expansion between 1.20% and approximately 1.6 to 1.9% may be produced. Likewise, increase in the amount of bromide will increase the expansion of any given base containing cristobalite.

A further advantage in the use of the bromides as a thermal expansion improving agent is the fact that molds containing same may be heated to temperatures of approximately 1500 to 1800° F., without experiencing unduly rapid shrinkage as is the case with many of the other expansion improving agents, and as is also true of the investment composition base itself. This is especially desirable inasmuch as alloys now used in dentistry made of base metals may be successfully cast in a mold that has sufficient expansion within the casting temperature range demanded by these higher fusing alloys and which temperature range often approaches as high as 1600 to 1800° F.

What is claimed is:

1. An investment composition for casting metals and their alloys, consisting principally of a refractory filler and a binder, in such proportions as to give an investment composition, and containing a soluble inorganic bromide, with such bromide being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 3%.

2. An investment composition for casting metals and their alloys, containing from 18 to 50% binder, from 82 to 50% cristobalite, and a soluble inorganic bromide, with such bromide being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 3%.

3. An investment composition for casting metals and their alloys, consisting principally of a refractory filler, some of which is in the form of cristobalite and a binder in such proportion as to give an investment composition, and containing a soluble inorganic bromide in such proportion to improve the expansion property of the composition, but not in excess of 3%.

4. An investment composition for casting metals and their alloys, consisting principally of cristabolite and quartz, and a binder in such proportion as to give an investment composition and containing a soluble inorganic bromide in such proportion as to improve the expansion property of the composition but not in excess of 3%.

5. An investment composition for casting metals and their alloys, consisting principally of a refractory filler and a binder, in such proportion as to give an investment composition, and containing a bromide selected from the group containing ammonium, potassium, sodium, rubidium, caesium, barium, calcium, lithium, strontium, magnesium, iron, zinc, nickel, cobalt, chromium, manganese, aluminum, cadmium-potassium, cadmium, copper, lead, bismuth, antimony, tin and hydrogen but not in excess of 3%.

6. An investment composition for casting metals and their alloys, consisting principally of a refractory filler and a binder, in such proportion as to give an investment composition, and containing a bromide selected from the group containing ammonium, potassium, sodium, lithium, rubidium, caesium, barium, calcium, strontium, magnesium, iron, zinc, nickel, cobalt, chromium, manganese, aluminum, cadmium-potassium, cadmium, copper, lead, bismuth, antimony, tin and hydrogen, in such proportion as to improve the expansion property of the composition, but not in excess of 3%.

7. An investment composition for casting metals and their alloys, consisting principally of a refractory filler and a binder in such proportions as to give an investment composition, and containing potassium bromide, with such bromide being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 3%.

8. An investment composition for casting metals and their alloys, consisting principally of a refractory filler, and a binder in such proportion as to give an investment composition, and containing ammonium bromide but not in excess of 3%.

9. An investment composition for casting metals and their alloys, consisting principally of a refractory filler and a binder in such proportions as to give an investment composition, and containing ammonium bromide, with such bromide being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 3%.

10. An investment composition for casting metals and their alloys, containing from 18 to 50% binder, from 82 to 50% cristobalite, and ammonium bromide, with such bromide being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 3%.

11. An investment composition for casting metals and their alloys, consisting principally of a refractory filler, some of which is in the form of cristobalite, a binder in such proportion as to give an investment composition, and containing ammonium bromide in such proportion to improve the expansion property of the composition, but not in excess of 3%.

12. An investment composition for casting metals and their alloys, consisting principally of a refractory filler and a binder in such proportions as to give an investment composition, and containing sodium bromide, with such bromide being present in a quantity sufficient to improve the expansion properties of the composition, but not in excess of 3%.

ROBERT NEIMAN.
ROBERT C. ERNST.
EDMUND A. STEINBOCK.