March 23, 1943. R. NEIMAN 2,314,626

INVESTMENT

Filed Oct. 3, 1939

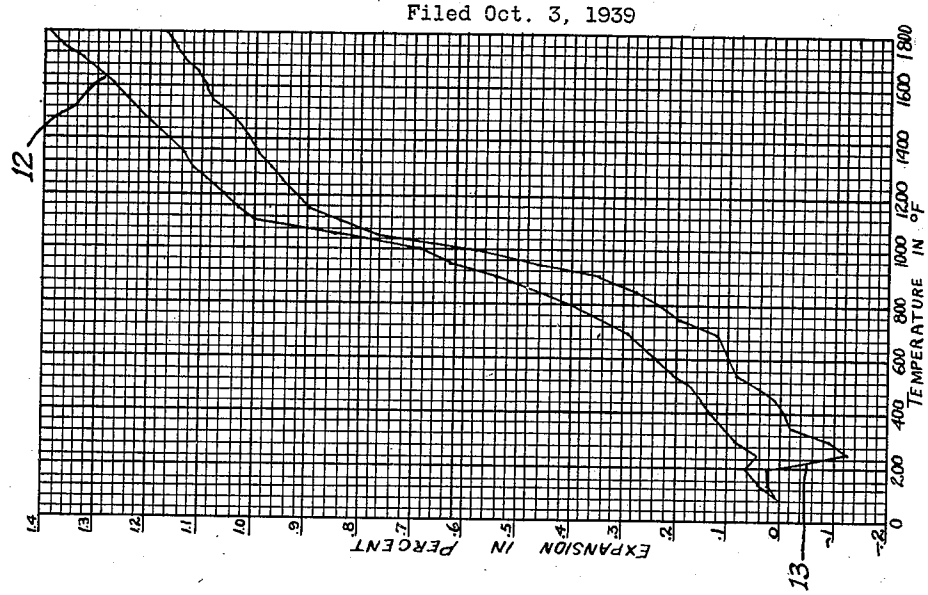


Fig. 2.

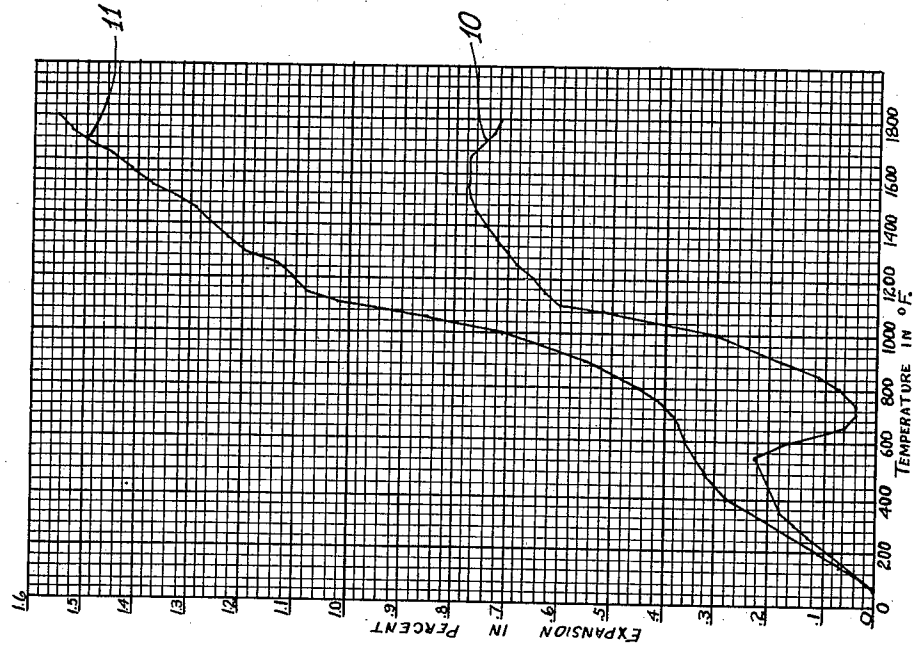


Fig. 1.

INVENTOR.
ROBERT NEIMAN
BY Joseph A. Rave
ATTORNEY

Patented Mar. 23, 1943

2,314,626

UNITED STATES PATENT OFFICE

2,314,626

INVESTMENT

Robert Neiman, Louisville, Ky., assignor to Edmund A. Steinbock, Louisville, Ky.

Application October 3, 1939, Serial No. 297,723

12 Claims. (Cl. 22—188)

This invention relates to investment compositions for making refractory molds into which metals, such as precious metals or other 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 from 800° 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, just 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 all mixtures of the above forms. All test results and curves, wherein the term plaster is referred to hereinafter, were made with alpha gypsum or Hydrocal, which, as mentioned above, is the preferred form.

The refractory filler as generally used consists principally of siliceous matter. Since the chief property, 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, possess high expansions along with good refractory properties, and in addition are 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, in fact several oxides, alone have unusually high expansions, due to change of phase or inversion. Whenever 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 char-

acteristics, 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 compositions do not have the desired thermal expansion in conjunction with proper strength, nor several other desirable characteristics. For example, a mixture of 30 parts plaster and 70 parts silica, and gaged with 29 parts of water will show an expansion of but .70% 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 those of 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 at 1600–1800° 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 a further object of this invention to provide an investment composition having a wide range of desirable expansions and secured by choosing a corresponding casting temperature.

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 the 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 may 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 illustrating the expansion of two investment compositions when heated under identical conditions.

As was noted above, general or simple investment compositions for dental and other purposes have been known and used for many years. This general composition has comprised from 18 to 50 per cent plaster and from 82 to 50% silica. The thermal expansions of such compositions increases 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 the drawing, the reference numeral 10 indicates the thermal expansion and contraction of a mixture of 30% plaster and 70% silica, and indicates a thermal expansion of .70% between room temperature and 1300° F. This investment was made with a water to powder ratio (W/P) of .29, that is, 29 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 set forth above is, from a commercial standpoint, about as low as is practicable.

In 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 ammonium nitrate for an equal amount of silica. In this composition, the W/P ratio was held as above, that is, .29. As will be seen, this resulted in a thermal expansion of 1.20% between room temperature and 1300° F., and up to 1.55% at 1800° F.

By comparison of the curves 10 and 11, it will be noted that the 1% of ammonium nitrate produced an investment composition that was, throughout the heating period, expanding regularly, while the other or simple investment composition twice alternated expansion and contraction. 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 in a mold heated to approximately 1300° F., and have a casting shrinkage of 1.25%. The ammonium nitrate composition, whose expansion curve is illustrated in the drawing, shows a thermal expansion of 1.20% at this temperature which is approximately enough to counteract the casting shrinkage of the gold. If exactly 1.25% is needed, a slightly greater amount of ammonium nitrate may be added or else the casting temperature may be raised to approximately 1375° F. The simple investment composition has but slightly over one-half of this expansion at the respective temperatures. In such cases, where base metals are to be cast, and whose casting shrinkages are generally about 1.5%, the ammonium nitrate composition illustrated in the drawing would give the desired expansion, and at approximately 1600° to 1700° F., which is the desired casting temperature for this type of alloy. Of course, where stronger molds may be needed, the binder may be increased, and with a subsequent increase of ammonium nitrate, will give the same desired expansion, but with greater mold strength.

As was noted above, other thermal expanding improving agents had been employed, such for example as sodium chloride and boric acid. It should be noted, however, that one percent of sodium chloride in place of the one percent zinc nitrate would give approximately only 1.0% expansion, while one percent of boric acid would

only give approximately .9% thermal expansion.

It has been found that increasing the amount of ammonium nitrate increases the thermal expansion of the investment composition, but not in direct proportion to the amount added. The greatest thermal expansion increase is obtained with the first unit of ammonium nitrate added to the composition, and subsequent units of ammonium nitrate added have a constantly decreasing increasing effect on the thermal expansion. At about 4 to 5% addition of ammonium nitrate, the increase in expansion is extremely slight, and this is approximately the upper limit of usefulness. These facts hold true regardless of the proportions of binder and refractory filler used within the investment proportions limit. This is of course true that as the proportion of silica is increased, with consequent decrease in proportion of binder, the expansion will generally be increased and similarly the reverse is true.

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 ammonium nitrate, 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. Some of the present sulfated higher alcohols, or similar existing compounds offer a slight advantage along this line.

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 30% plaster with 1% ammonium nitrate and 69% 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 1.5 to 2.1%, 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 30% plaster and 1% ammonium nitrate, and with varying amounts of quartz and cristobalite, any thermal expansion between 1.20% and approximately 1.5 to 2.1% may be produced. Likewise, increased in the amount of ammonium nitrate will increase the expansion of any given base containing cristobalite.

A further advantage in the use of the nitrates as a thermal expansion improving agent is the fact that molds containing same may be heated to temperatures of approximately 1600–1800° 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.

It has been found that the addition of small amounts of nitrates will materially increase the thermal expansion as well as other desirable properties of investments. It is indeed phenomenal to find that all nitrates available will do this. This condition has been found to exist with respect to all of the nitrates listed below. Other soluble, inorganic nitrates were not commercially available at the time tests were made; however, it would be fairly safe to predict that this action would be similar to those in the list.

The list given below divides the inorganic nitrates into three groups. This grouping is based on general chemical similarity. In each group the nitrates are arranged in the approximate order of effectiveness in increasing the thermal expansion of the investment. For example, the top elements in each group give an expansion of approximately 1.20% at 1300° F. when added in the proportion of 1% by weight (calculated on the anhydrous basis) to a base containing 30% plaster and 69% silica (ground quartz). The succeeding members of each group have a slightly lesser effect of increasing the thermal expansion. The lowest members of groups I and II will give an expansion of approximately .95% at 1300° F., while the lowest members of group III will give approximately .75% expansion at 1300° F. Wherever possible the nitrate was powdered and added to the dry powder base. Where this was impossible, the nitrate was dissolved in 29 ml. or water, which amount was always mixed with 100 gms. (includes weight of nitrate) of powder, in order to make accurate comparison possible. Increasing the proportion of water decreases the expansion, and decreasing the water increases the expansion to a small extent. Since many of the nitrates are purchased in a hydrated form, it was impossible to add exactly 1% based on the anhydrous form, inasmuch as the degree of hydration is not always accurately represented by the formula amount of water of hydration. This slight difference, coupled with the fact that many values in the table are very close together and often of a smaller increment than the absolute accuracy of the instruments or dilatometers used for measuring the expansion, the inventor does not wish to limit himself to the exact order.

The following table gives the approximate order of effectiveness of the nitrates when using 1% of each of the simple base described above.

I	II	III
Ammonium	Copper	Cerium
Magnesium	Zinc	Beryllium
Lithium	Manganese	Lanthanum
Strontium	Nickel	Thorium
Calcium	Cadmium	Erbium
Barium	Aluminum	Yttrium
Sodium	Cobalt	Thallium
Potassium	Chromium	Uranium
Rubidium	Iron	Palladium
Caesium	Bismuth	Zirconium
Hydrogen	Silver	Tellurium
	Lead	Titanium

The base material has a thermal expansion of .70%. Rubidium, caesium and hydrogen (nitric acid) tested in smaller quantities, and therefore not listed. Mercury not tested, due to poisonous vapors. All other nitrates unknown or unavailable at time of tests.

I am aware that high percentages of the heavy metal nitrates have been recommended as pro-

tective agents, due to decomposition into their respective oxides. Since the claimed large amounts of nitrates owe their effect as above to the oxides formed, it was decided to try several oxides. These were of little or no value for expansion. Since many of the nitrates promote investment expansion to as high as 1800° F., it was decided to determine whether this was due to the oxide formed. This possibility was immediately eliminated when ammonium nitrate (1%) promoted investment expansion to above 1800° F., this in spite of the known decomposition of ammonium nitrate into gaseous products at 410° F. and leaving no protective non volatile residue. From this, it must be concluded that nitrates are most effective and useful in small amounts and owe their property to their chemical or physical action while in the nitrate form, and at low temperatures during the early formation of the mold.

Fig. 2, reference numeral 12, shows the expansion of an investment containing 5% of copper nitrate, 20% plaster, and 75% silica. Reference numeral 13 is a similar composition, but containing only 1% of copper nitrate, 20% of plaster, and 79% silica. This is a typical example of the more than beneficial effect of small percentages and the actually deleterious effect of large percentages of copper nitrate, for example. In fact, with the large percentage of copper nitrate, the curve had quite a shrinkage in the low range, and would not, therefore, pass the present American Dental Association specification No. 4 for inlay investments. It is, therefore, recommended that small percentages of group II nitrates be used, and that perhaps 3% by the upper limit with these nitrates of group II.

It is further interesting to note that most nitrates are accelerators and will make it possible to cut down or eliminate other accelerators. On the other hand, cerium, erbium, and lanthanum nitrates are retarders. Thus an accelerator, a retarder, or both may be combined in controlling the setting characteristics, along with expansion properties. The base used for all experiments shows an expansion of .7% at 1300° F. This is increased by all of the various nitrates. One percent of ammonium nitrate will just about double the expansion. It is perhaps the most powerful expanding agent known (per unit weight). By choosing various nitrates or varying their amounts, an almost unlimited range of expansion characteristics is posisble. Furthermore, it is of course possible to add other ingredients as is known in the art, such as graphite, plasticizers, protective agents, cleansing agents (such as chlorides), etc.

Some of the nitrates, especially barium, strontium, potassium, sodium and silver are sufficiently non-hygroscopic to permit use in their powdered form, along with the other powdered base ingredients. Other nitrates may be used likewise under proper packaging conditions, but it would be preferred that they be added to the gaging water in solution. This may seem, at first, to be a serious disadvantage, especially from the manufacturer's standpoint; it does, however, open up a new type of possibility and technic.

In spite of the fact that the casting shrinkage of gold and its alloys is stated to be 1.25% regardless of shape or size, it has been nevertheless the need and doings of manufacturers to work out various technics to permit achieving various expansions with the same investment, which, because it already contained a given amount of expanding agent, did not permit variation by the user. The latter could vary the amount of gaging water, but this would weaken or destroy the working properties of an otherwise properly proportioned investment composition.

With the nitrates, the manufacturer can furnish a powder base of standard composition and a liquid containing one or more nitrates in solution. He can then furnish a chart and directions for diluting this given solution in order to achieve any of a large possibility of expansion values. With ammonium nitrate, in varying amounts and with the choice of varying casting temperatures, one can achieve anywhere from .7% to 1.5% or better. No technic or material yet known has offered such wide range of possibilities in such simple and accurate manner.

As stated above, the nitrates are accelerators in general, and therefore if the concentration is varied, the setting time will be varied. The inventor proposes that a retarder be put directly into the nitrate solution (preferably a concentrated one), by the manufacturer. Thus, when more of the nitrate solution is used, more retarder is used, and the result is a balanced setting time regardless of expansion. It is of course understood that the user does not use the desired amount of concentrated nitrate solution with a given powder amount, as this would often furnish insufficient amount of gaging liquid.

The user is furnished directions for diluting the original concentrates solution with given amounts of water. For example, if 29 ml. of original solution contained sufficient amount of nitrate to give a 2% nitrate content when mixed with 100 gms. of powder base, he can mix 14½ ml. of the original solution with 14½ ml. of water and have a 1% nitrate content.

The above technic can be used with other materials, but is especially desirable with nitrates and further makes the use of nitrates one giving almost unlimited possibilities of expansion control. This technic and the combination of an expander, an accelerator and a retarder is entirely new and unknown in the art.

Since the nitrates generally decompose at a low temperature their gaseous decomposition products are not as harmful as decomposition products given off by other investment expanding agents at much higher and therefore more active temperatures. Wherever provision is made for removing the decomposition products, this will carry along the wax vapors and at high temperatures there is little need for removing decomposition products. This saves wear and tear on the muffle of the furnace and on surroundings. Furthermore, there is no need to soak the mold for hours at high temperatures (1500–1800° F.) in order to rid the mold of the expanding agent, thus saving considerable time.

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 nitrate, with such nitrate being present in a quantity sufficient to improve the expansion properties of the composition, but not in excess of 5%.

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 nitrate, with such nitrate being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 5%.

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 nitrate in such proportion to improve the expansion property of the composition, but not in excess of 5%.

4. An investment composition for casting metals and their alloys, consisting principally of cristobalite and quartz, and a binder in such proportion as to give an investment composition, and containing a soluble inorganic nitrate in such proportion as to improve the expansion property of the composition, but not in excess of 5%.

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 nitrate selected from the group containing ammonium, potassium, sodium, lithium, rubidium, caesium, barium, calcium, strontium, magnesium, iron, zinc, nickel, cobalt, chromium, manganese, aluminum, cadmium, copper, lead, bismuth, hydrogen, silver, cerium, beryllium, lanthanum, thorium, erbium, yttrium, thallium, uranium, palladium, zirconium, tellurium and titanium, but not in excess of 5%.

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 nitrate selected from the group containing ammonium, potassium, sodium, lithium, rubidium, caesium, barium, calcium, strontium, magnesium, iron, zinc, nickel, cobalt, chromium, manganese, aluminum, cadmium, copper, lead, bismuth, hydrogen, silver, cerium, beryllium, lanthanum, thorium, erbium, yttrium, thallium, uranium, palladium, zirconium, tellurium and titanium, in such proportion as to improve the expansion property of the composition but not in excess of 5%.

7. 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 barium nitrate, with such nitrate being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 5%.

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 zinc nitrate, but not in excess of 5%.

9. 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 zinc nitrate, with such nitrate being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 5%.

10. An investment composition for casting metals and their alloys, containing from 18 to 50% binder, from 82 to 50% cristobalite, and zinc nitrate, with such nitrate being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 5%.

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 zinc nitrate in such proportion as to improve the expansion property of the composition, but not in excess of 5%.

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 magnesium nitrate, with such nitrate being present in a quantity sufficient to improve the expansion property of the composition, but not in excess of 5%.

ROBERT NEIMAN.