July 5, 1966 H. C. STALLMAN 3,259,492

THALLIUM-ZINC-LEAD -MERCURY ALLOYS

Filed March 24, 1965

FIG. 1.

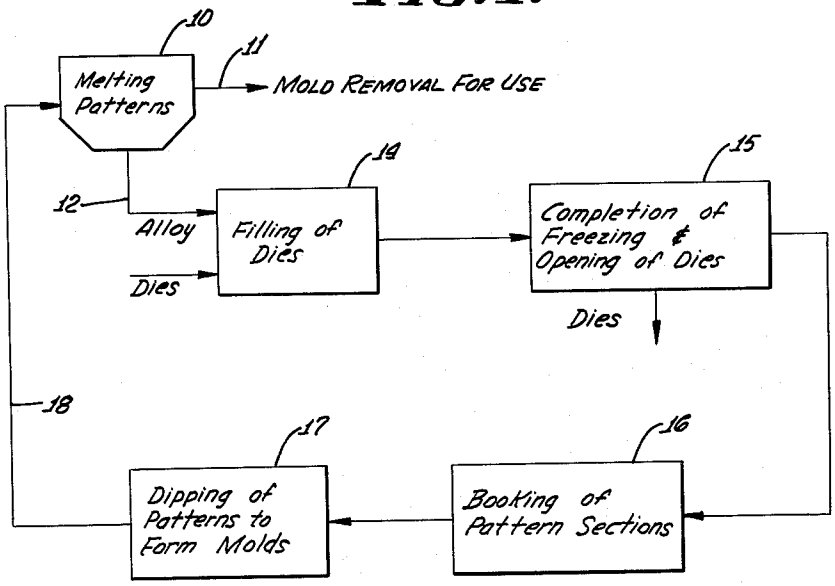
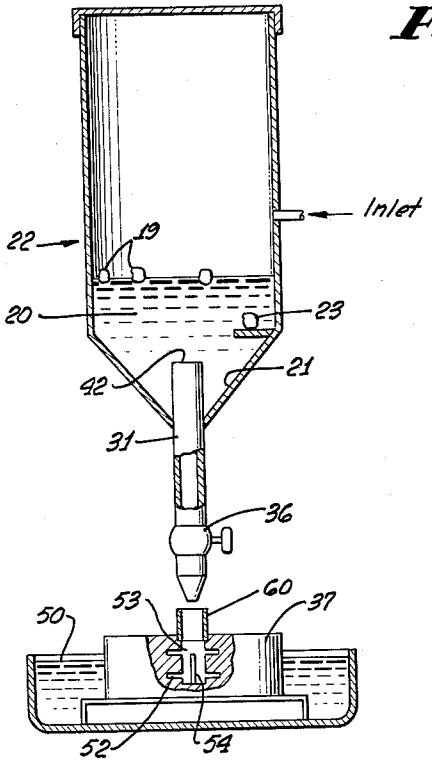


FIG. 2.



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United States Patent Office 3,259,492 Patented July 5, 1966

3,259,492
THALLIUM-ZINC-LEAD-MERCURY ALLOYS

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Filed Mar. 24, 1965, Ser. No. 442,404
6 Claims. (Cl. 75—169)

This is a continuation-in-part of application Serial No. 253,173, filed January 22, 1963, now abandoned.

This invention relates generally to the art of forming and using impermanent investment casting patterns, and more particularly concerns novel alloy compositions and methods for forming and using patterns made therefrom.

U.S. Patent 2,857,641 describes the desirability of using intermetallic compounds of mercury and thallium for forming investment casting patterns. An alloy was indicated that is close to the thallium-mercury eutectic composition, Tl_2Hg_5, which contains 28.95 percent by weight of thallium and which starts to freeze at about 56 degrees F. and which is solid within one degree range. No other metallic composition that freezes so slightly below ordinary room temperature was then available. This alloy was attractive for the indicated use because of the potentially low refrigeration requirement. However, thallium oxidizes readily and the oxide is very soluble in water, forming an alkaline hydrate solution that is a good conductor. Thallium is electro-positive to most common metals and decidedly so to mercury. The patent specifies the use of a protective liquid covering to suppress oxidation of the thallium and suggests ethylene glycol as the preferred liquid. But, under use conditions atmospheric moisture is condensed on metal parts and is absorbed by the ethylene glycol bringing free oxygen into contact with the alloy and starting the above chain of events.

As a result, the protective fluid soon had to be replaced. Depletion of thallium from the alloy made it necessary to replace the expanded thallium frequently and chemical analyses and computations had to be made to determine the amount of thallium to add each time. Since ethylene glycol costs about $4.50 per gallon and thallium costs about $12.50 per pound, the maintenance costs were very high relative to any potential savings in refrigeration costs. Further, as the thallium became depleted the frozen patterns made from it became increasingly difficult to book securely. The term "booking" as used herein is intended to described a physical characteristic of mercury alloy which results in a completely dependable bond between any two clean surfaces of the frozen alloy which are brought into contact with or without the application of pressure.

The state of the art has been recently advanced by addition to the alloy of other metallic substance such as zinc which is electro-positive to thallium. It was determined that zinc preferably should be present in dissolved state in the alloy and in amount sufficient to inhibit oxidation of the thallium.

The present invention further advances this art in that it has now been found that the addition of small amounts of lead to the mercury, thallium and zinc alloy results in improvements in tensile strength of the frozen pattern, in its stress capabilities, in its frozen crystal characteristics, particularly as respects complete filling of small voids in the master molds, in its resistance to oxidation and hydrolization, in its improved booking characteristics, and in its freezing time span. It has been found that the lead component extends the freezing range and hence freezing time of the alloy, which is of particular importance because pressure may be best applied to the alloy in this semi-frozen or slushy stage. That this characteristic is of advantage can be seen when it is realized

that too rapid freezing of alloy during pouring thereof into the mold may result in incomplete filling of small voids in the mold, with consequent loss of mold detail in the resultant pattern. The application of pressure to alloy in the mold exerts a force equally distributed over all surfaces interior to the die cavity, including those of green strength ceramic cores, preventing their destruction or dislocation.

These and other objects of the invention as well as the details of an illustrative embodiment will be more fully understood from the following detailed description of the drawing, in which:

FIG. 1 is a flow diagram illustrating the use of the alloy; and

FIG. 2 shows the manner in which the alloy may be kept for maintenance of correct composition, and for delivery of pure alloy at any desired time.

Referring first to FIG. 1, typically the alloy withdrawn or delivered at **12** is used to fill dies or master molds which have previously been chilled to a temperature below the freezing point of the alloy as a means of its more rapid solidification. The alloy contained in the dies is then frozen as indicated at **15**, after which the die is opened and the frozen alloy pattern sections removed. The latter then may or may not be treated with a suitable flux for purposes of facilitating ready booking of the pattern sections as indicated at **16**, the patterns then being rinsed free of excess flux solution, if any.

Finally, the booked patterns are used to form molds at **17**, and typically the patterns are dipped into a refractory slurry to build up successive layers or coatings on the frozen alloy pattern. Typical slurry compositions are disclosed in U.S. Patents 2,182,692, 2,820,266 and 2,820,268 to E. F. Kohl, and 2,790,218 and 2,749,586 to E. F. Kohl, et al. After green curing, the molds and patterns are then transferred at **18** to a melting chamber at **10** in FIG. 1 (**22** in FIG. 2) wherein the frozen alloy is melted out of the molds. The molds are then withdrawn as indicated at **11** for subsequent firing and use in casting, and the melted alloy is removed at **10** for reuse in the process.

The thallium content of the alloy is protected against oxidation by the addition to the alloy of a metallic substance such as zinc that is electro-positive to thallium. In this regard, the quantity of thallium present in the alloy is sufficient to elevate the freezing temperature of the alloy well above the freezing temperature of mercury alone, and typically the thallium content will approximate the stoichiometric content of the eutectic intermetallic alloy Tl_2Hg_5 containing 28.95 percent by weight of thallium. This alloy freezes solidly at about 56 degrees F., which is within the range of ordinary refrigeration making the alloy attractive for commercial use.

The zinc dissolved in the alloy may be about 3 percent by weight when prepared at or near the boiling point of water, but at ordinary room temperatures it is typically close to 0.6 percent by weight or less, in the fluid alloy, this content being maintained in the process by the addition of solid state zinc particles as shown at **19** in FIG. 2 to the liquid alloy pool **20** formed in a sink **21** of chamber **22**. With zinc in solution in the alloy, thallium is protected against oxidation and dissolution, and no oxidation suppressing organic liquid such as ethylene glycol is needed. Any oxidation of zinc is insignificant.

In accordance with the invention, lead is also dissolved in the alloy in amounts between 0 and 3.0 weight percent of the alloy, but preferably at about 2.0 percent at dispensing temperatures just above the temperature at which freezing starts. For this purpose, lead pieces **23** may be kept in the pool **20** for maintaining the latter in balanced solution. In this regard, the amount of zinc or lead is indicated to be excessive when it crystallizes out of solu-

tion on freezing, preventing booking. This condition may be cured by adding a 1 percent solution of nitric acid or it may be prevented by using bar form zinc or lead to reduce surface exposure to the mercury and thallium solution.

The alloy liquid in the pool **20** may be withdrawn from the chamber **22** through suitable valve apparatus as shown at **36**, whenever it is desired to fill the master mold **37** chilled by the liquid bath **50**. Discharge line **31** has an entrance **42** within the interior of the pool **20** so as to be spaced from the chamber walls at which any impurities tend to collect.

In freezing tests conducted upon a number of batches of mercury-thallium-zinc-alloy containing between 26.7 percent and 40.3 percent thallium, with the balance mercury containing 1 percent zinc, it was found that the alloys with relative wide freezing temperature range of 13 degrees F. or over, that is the alloys containing 32.0 percent thallium and greater, have rough spots or "tears" of extruded alloy on the surface of the patterns, these rough spots being the last to freeze. Furthermore, if such alloys are used for making molds, the castings resulting from use of the molds have a rough surface.

Also, it was found that pattern sections containing 27.9 and less weight percent thallium not only have a freezing temperature range of 9 degrees F. and greater, but also exhibit inferior booking properties. For example, whereas the alloys having freezing ranges of no more than 6 degrees F. may be booked firmly without external pressure applied to the test pieces, it is necessary to apply external pressure to the test pieces in order to book them when such pieces contain thallium outside the preferred freezing temperature range of no greater than 6 degrees F.

By the addition of lead as disclosed, it is possible to realize the advantages of wider freezing temperature ranges and slower freezing, as well as alloy chemical stability and increased capacity to penetrate small voids in master molds, and also retain good booking properties. Thus, an alloy containing about 31.6 percent thallium, 0.7 percent zinc, 2.0 percent lead and the balance mercury will start to freeze at about 51 degrees F. and completely freeze at about 45 degrees F., whereas in the absence of lead addition, the alloy will freeze much faster, starting at about 51 degrees F. and completely freezing at 49 degrees F. Accordingly, the lead addition enables mold filling under conditions such that the freezing step is only partially completed while the alloy is introduced into the mold, whereby there is time for the weight of the alloy filled into the upper interior of the mold and in riser **60** to force the incompletely frozen alloy in the interior of the mold cavity into the small voids defining the pattern detail, and indicated at **52**, the mold cavity **53** also containing a green strength ceramic core **54**.

Also, the addition of lead increases the strength characteristics of the frozen alloy, as indicated by the following tests:

TRANSVERSE BENDING TESTS OF FROZEN ALLOY BARS—AVERAGE BENDING OF THREE TEST BARS

Alloy Number	At 40° F.	At 19° F.
21. Eutectic ---------- degrees	109	63
22. Zn added ---------- do	82	25.7
25. Zn and Pb added ---------- do	37.2	21.7

Finally, the alloy of mercury, thallium, zinc and lead is essentially non-oxidizing enabling the use of a process wherein the molds may be kept dry at the time they are filled with alloy to give a surface quality to the solidified

pattern which compares almost exactly with the quality of the mold interior surface. This obviates the need for wetting the mold interior surface with a solution preventing oxidation of alloy, such a wetting film acting to reduce the surface quality of the solidified pattern.

What is claimed is:

1. An improved mercury alloy mold pattern composition consisting of 26 to 32 percent by weight thallium, zinc present in an amount effective to substantially eliminate oxidization of the thallium, lead present in an amount to extend the freezing range of the alloy composition and the balance essentially all mercury.

2. An improved impermanent mold pattern composition consisting of 26 to 32 percent by weight thallium, zinc in an amount effective to reduce the oxidization of the thallium, said zinc being less than 3 percent by weight lead in an amount effective to increase the strength of the composition and being less than 3 percent by weight, lead, and the balance essentially all mercury.

3. An improved impermanent mold pattern composition consisting of thallium in an amount sufficient to elevate the freezing temperature of the alloy well above the freezing temperature of mercury alone, zinc in an amount sufficient to inhibit oxidation of the thallium, lead in an amount sufficient to increase the strength of the composition, said lead being present up to 3 percent by weight and the balance essentially all mercury.

4. An improved mercury alloy mold pattern composition consisting of thallium in an amount sufficient to elevate the freezing temperature of the alloy into a range of about 6 degrees F. and well above the freezing temperature of mercury alone, zinc in an amount sufficient to inhibit oxidation of the thallium, lead in amount sufficient to extend the freezing range of the alloy and being present up to 3 percent by weight, and the balance essentially all mercury.

5. A pattern composition for forming an impermanent pattern, said composition consisting of a pool of liquid mercury and 26 to 32 percent by weight liquid thallium, lead and zinc, at least a portion of said lead and zinc being in solid form in the pool to maintain an equilibrium with the lead and zinc in the composition to thereby retain the pool in balanced condition for use as an impermanent pattern material in the manufacture of investment castings.

6. A pattern composition for forming an impermanent pattern, said composition consisting of a primary alloy of mercury, thallium, zinc and lead in a liquid pool, and lead and zinc solids in the pool to maintain the pool in balanced condition for use as an impermanent pattern material in the manufacture of investment castings, the alloy consisting of between 26 to 32 percent by weight thallium, up to 3 percent by weight zinc, said zinc being present in an amount effective to substantially prevent oxidation of the thallium up to 3 percent by weight lead, said lead being present in an amount effective to extend the freezing range of the alloy, and the balance mercury.

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