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G. M. BOUTON ET AL

2,425,725

METHOD OF CASTING AND RAPID ANALYSIS OF ALLOYS

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FIG. 1

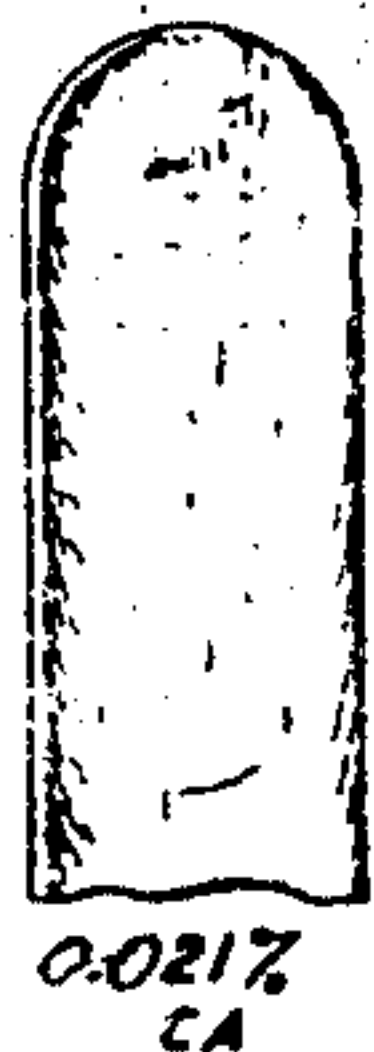


FIG. 2

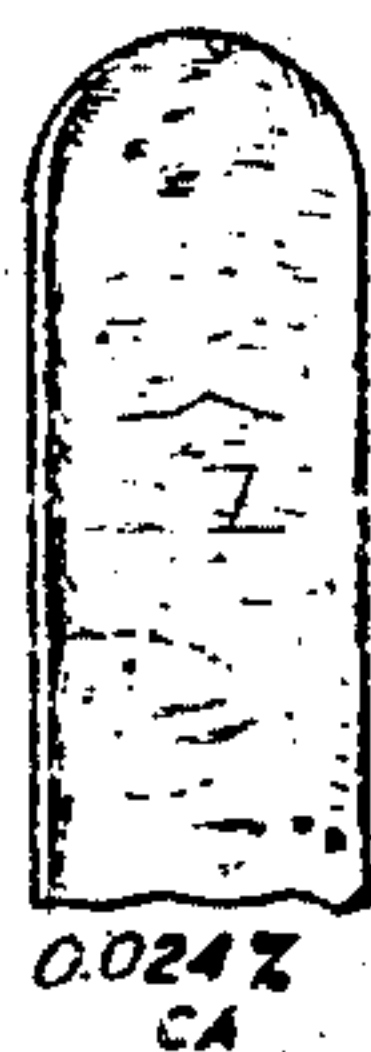


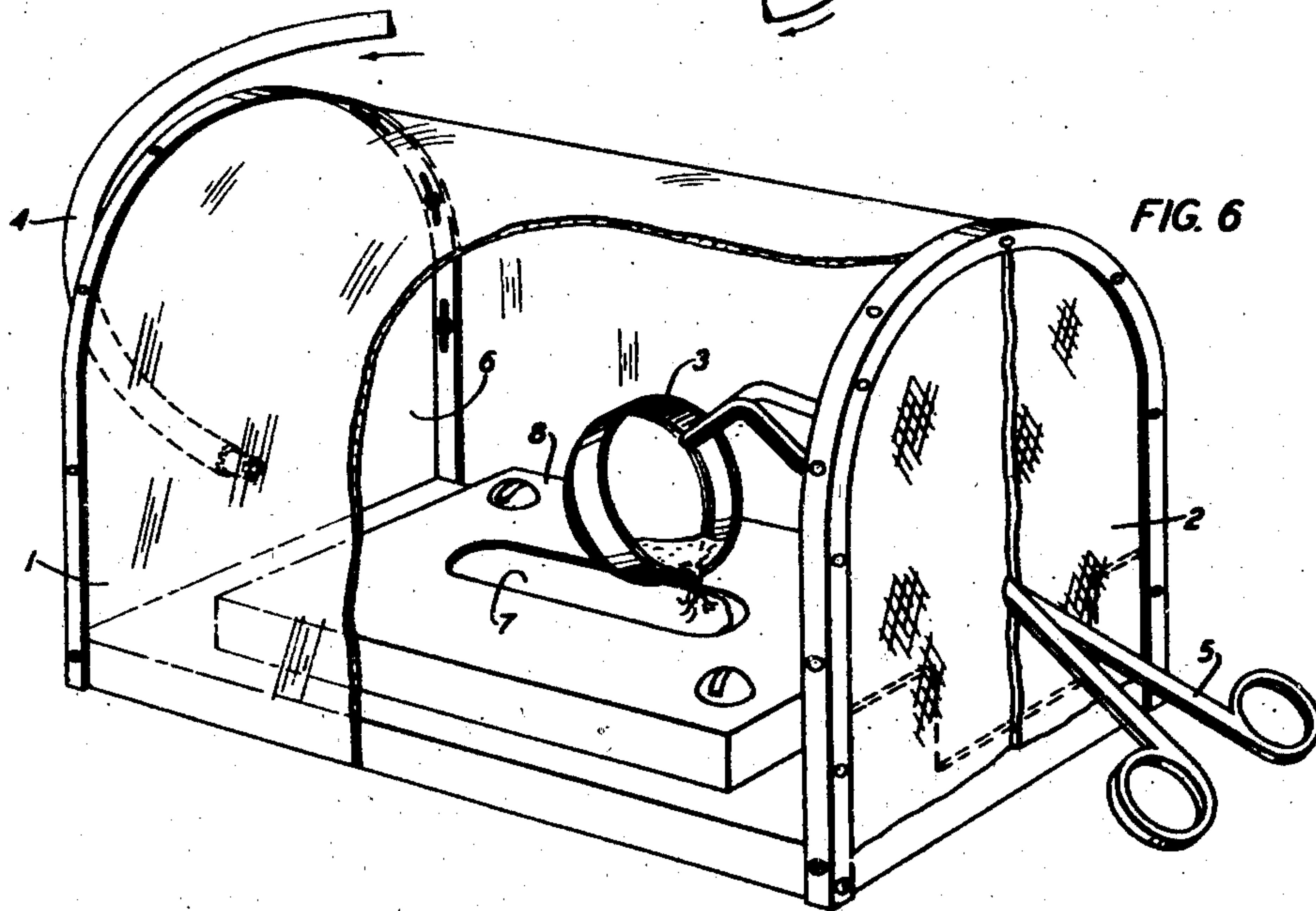
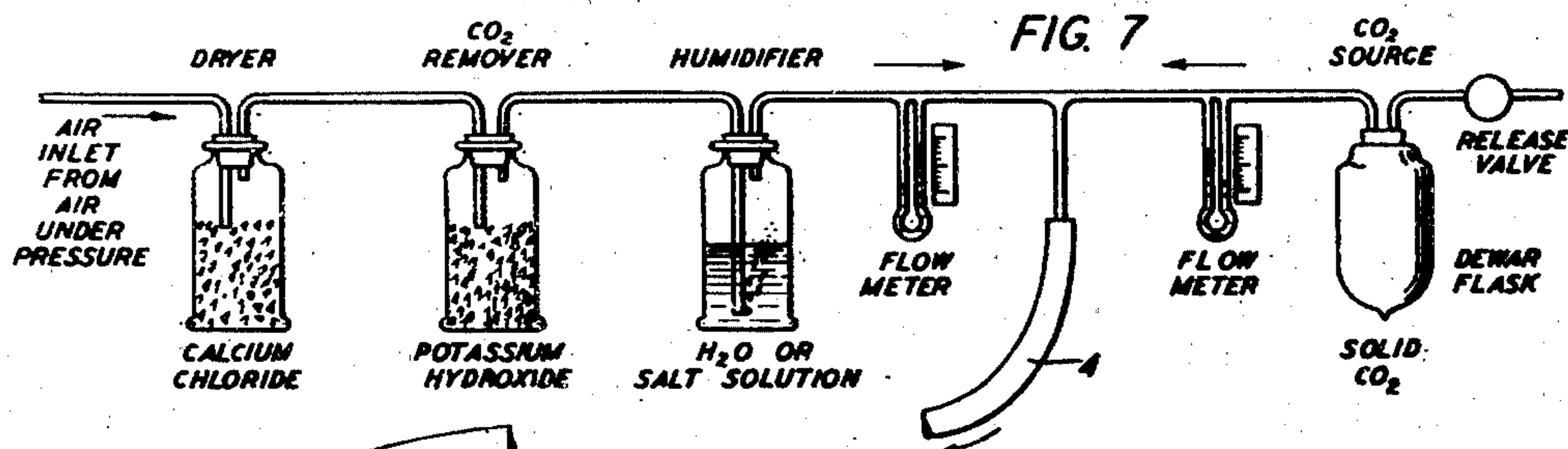
FIG. 3



FIG. 4



FIG. 5



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METHOD OF CASTING AND RAPID
ANALYSIS OF ALLOYS

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4 Claims. (Cl. 22—214)

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This invention relates to methods of and apparatus for quickly and in a commercially satisfactory manner estimating or determining the amount of alloying material in lead alloys, more specifically, the amount of calcium in lead.

In particular, the invention relates to the control of calcium content in lead-calcium manufactured articles, especially cable sheath and an object is to provide processes and means for accomplishing a determination of the calcium content with the necessary accuracy and with sufficient rapidity that the control may be exercised in a commercially feasible and economically advantageous manner.

The invention is based, in part, upon the discovery that the per cent of calcium in lead-calcium alloys may be estimated within close limits of accuracy by visual inspection and, in part, that the efficacy of this visual method of estimation depends upon casting the ingots used for estimation in a controlled atmosphere, more specifically, an atmosphere in which the percentage of carbon dioxide and the relative humidity or moisture content are controlled and regulated.

From a generic aspect the invention relates to a technique of metallurgical analysis by which the constituents of metallic compositions or compositions composed chiefly of metal may be determined by casting samples of the metal under a controlled and regulated atmosphere and comparing the resultant castings with samples or series of samples cast under a similar atmosphere; obviously the method is applicable only in those cases wherein the composition assumes a superficial appearance, when cast in a particular atmosphere, which is a function of the composition or the amount of some constituent therein; furthermore, by a regulated atmosphere is meant an atmosphere of which the constituents are regulated to the required degree which in the case of atmospheres containing the constituents of ordinary air signifies a degree of regulation such that the constituents are controlled to such an extent that their variations are much smaller than the variations of natural air as found in rooms and outdoor places; this specification and appended claims are to be read in the light of these considerations.

In a specific embodiment as applied herein the

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invention is exemplified in a process desirable for use in connection with a particular form of lead-calcium cable sheath composed of commercial lead with a desired calcium content of 0.028 per cent plus or minus .005 per cent. For the particular purposes for which this cable is to be used this percentage of calcium gives the most desirable combination of properties.

Emphasis is laid upon the rapidity with which the method of the present specification may be performed; methods of the highest accuracy would be of very little use in calcium content control in industrial operations wherein a continuous and reasonably rapid manufacture of products is demanded because it is impractical to hold a kettle of alloy molten for a long time in order to await the calcium determination.

Thus in cable manufacture a method previously used consumed from one to two hours from the time of taking samples until the reporting of the result. This procedure was costly and, moreover, resulted in a lag in control so great that the calcium content of the finished product on some occasions fell outside the specified limits and caused a rejection of certain lengths of cable.

Since calcium is a very active element chemically, special manufacturing procedures have been developed to minimize the contact of molten lead-calcium alloy with the air. Despite the improved techniques, some calcium is always lost and must be replaced. Before this can be accomplished satisfactorily, obviously, the calcium content of the alloy must be determined. Conventional chemical procedures are accurate but unsatisfactory for plant control use because they are time consuming and too costly. The best of the chemical methods introduces a lag of at least two hours in control of the contents of the lead melting kettle. Quantitative spectrographic analysis methods were carefully tested, and while they showed some advantage over conventional analyses, they were still unduly time consuming.

This need for control has been manifest during some ten or twelve years of use of lead-calcium alloys for cable sheath. See Dean Patent 1,890,013, dated December 6, 1932, on application filed June 29, 1928. With the increasing usage in lead-calcium alloys for cable sheath, storage-battery grids, and other applications, the need for a rapid, reliable and not too costly method

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for determining the calcium content has been urgent. In approaching the problem, several methods involving physical, chemical, or electrical properties of lead-calcium alloys were investigated. These methods proved inadequate. Either the properties involved were insufficiently sensitive to changes in calcium content, or other factors masked the effect of calcium variations.

The more specific aspect of the present invention is related to the observation that molten lead alloys containing calcium in the range over a few hundredths of a per cent quickly film over with an oxide coating. Observation of the characteristics of these molten alloys revealed no phenomena that varied sufficiently with calcium content to serve as a clue to the composition. When such alloys are chill cast with as little agitation as possible, the surface of the ingots becomes progressively duller with increasing calcium content to a certain value. Further increase in calcium content results in the fissuring of the surface oxide leaving bright metallic areas exposed. This fissuring phenomenon is the basis of the composition-sensitive indication employed for present purposes. When samples of lead-calcium are melted and cast under properly controlled conditions the surface markings for a particular composition are reproduced with considerable fidelity in respect to areas of dull and bright surface. The ratio of these areas is dependent on the calcium content.

The conditions found necessary or desirable are, first, the molten test sample is exposed to the open atmosphere for the least possible time; a second, the alloy should not be stirred nor the crucible shaken to any substantial extent during the casting operation; third, the heat is removed from the crucible quickly after the last portion of the sample has melted; fourth, the atmosphere of the casting chamber must be controlled as to its carbon dioxide content and moisture content.

Further explanation has reference to the following drawings in which:

Figs. 1, 2, 3, 4 and 5 represent as nearly as we have been able to represent in drawings the surface appearance of test ingots cast according to the methods of the invention and containing essentially pure lead with calcium in the respective amounts of 0.021 per cent, 0.024 per cent, 0.026 per cent, 0.028 per cent and 0.030 per cent;

Fig. 6 represents a transparent walled casting chamber used to cast test ingots; and

Fig. 7 represents diagrammatically the apparatus employed for supplying a controlled atmosphere to the casting chamber of Fig. 6.

Control of the atmosphere over the surface of test castings has been found necessary to insure reproducible results. For this reason the Cellophane enclosed casting chamber 1 with a wooden or other suitable floor shown in Fig. 6 is used. There is a door 2 on the right-hand side for insertion of the crucible 3 and a rubber inlet tube 4 on the left for supply of the gas mixture. The end 6 of the chamber may consist of metal or any other suitable material, as may all of the chamber except a transparent window. Door 2 may comprise flaps of non-combustible sheet material. A tongs 5 may be employed to insert the crucible to pour a mass 7 of metal upon a metallic mold 8. This apparatus is quite simple and may be quickly and conveniently constructed to practice the method. We have found that both the moisture and the carbon dioxide content of the air influence the results obtained. Therefore, both are removed chemically and then reintro-

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duced in metered quantities to the air passing into the casting chamber. By means of appropriate flow meters, dry air could be mixed in definite proportions with air saturated with moisture to produce the desired humidity. Another and perhaps simpler system is to pass the dry air over salt or other solutions of known vapor pressure. Carbon dioxide is conveniently made available by placing solid carbon dioxide (dry ice) in a Dewar flask having a stopper with two exit tubes. By means of an escape valve on one tube any desired CO₂ pressure can be built up in the flask to force the gas through a flow meter and into the air line leading to the casting chamber. One satisfactory arrangement of apparatus for controlling the composition of the atmosphere is diagrammed in Fig. 7.

Fig. 7 with its applied legends is largely self-explanatory. From a suitable air inlet of air supplied under pressure the air is dried over calcium chloride, deprived of CO₂ over anhydrous potassium hydroxide, and humidified over a solution of vapor pressure known for the temperature employed. Solid CO₂ furnishes gas and an escape or release valve permits regulation of the pressure. The air flow and flow of carbon dioxide are measured by flow meters of any suitable known type and combine to pass to the chamber 1 through tube 4 to produce a constant supply of uniform atmosphere.

The success of the method is largely dependent on the details of procedure given below. Since calcium is readily removed from lead by oxidation, a melting and casting procedure for the test specimens is used which results in a minimum loss of calcium. Fluxes and inert atmospheres, which normally provide adequate protection against oxidation are not used here because they interfere with the fissuring phenomenon that is the basis of the method.

The procedure, in detail, comprises melting a piece of the cable sheath or other material to be tested in the hemispherical sheet iron crucible 3 which is about two inches in diameter. A Bunsen burner flame of sufficient intensity to melt a 100 gram sample in two minutes is applied to the crucible. The bottom edge of the sample melts first and the balance of the sample slides smoothly into the pool of metal first formed with a minimum of rupture of the surface. The broad round shape of the crucible permits it to be tilted until the lip is but a fraction of an inch from the surface of the mold before the metal starts to pour, thus subjecting the stream of molten alloy to only a brief exposure to the atmosphere during pouring. The molten alloy should never be stirred nor should the crucible be shaken unnecessarily during the casting operation. Under the melting conditions described, the casting temperature of the melt is controlled sufficiently if the crucible is removed from the flame three or four seconds after the last portion of the sample has melted. By a slight modification of procedure, samples for analysis may be taken directly from commercial melting kettles. The shape or size of the mold used does not appear to be critical. We use an iron plate 1.9 cm. x 10 cm. x 20 cm. with a tapered depression milled in its surface. The test ingot is about 10 cm. long, 1.56 cm. wide and 0.06 cm. thick at the casting end and 0.95 cm. thick at the other end. It weighs 80 to 100 grams. The effect of mold temperature does not appear to be critical in the range from room temperature to that reached by the mold

as a result of casting into it at intervals of a few minutes.

Figs. 1 to 5, inclusive, disclose the surface appearance of chemically pure lead-calcium alloys cast in an atmosphere containing 0.02 per cent CO₂ and of 50 per cent relative humidity. In Fig. 1 there are no dark areas and in Fig. 5 the dark areas are close to 50 per cent of the surface. These dark areas in the actual specimens are actually very bright surfaces when viewed by directly reflected light. Increasing the carbon dioxide or decreasing the moisture content causes the bright surfaces to become more extensive and vice versa. This provides a few thousandths of a per cent latitude in adjusting the sensitive range of the method to the median calcium content desired. To an extent alloys having calcium contents somewhat outside the range of the method may be estimated by admixture with known amounts of lead-calcium alloys of known calcium content. Pure lead, in general, cannot be used for dilution because the oxide and possibly traces of impurities present in it cause the loss of some calcium from the mixture.

It has been found possible to make determinations by casting test pieces in open air and determining their content and then using these to determine the calcium content of samples cast in air of similar composition. This method subjects one to the necessity of analyzing new test pieces frequently but a more cogent difficulty resides in the fact that air, and particularly the carbon dioxide and water vapor content thereof, is or are subject to relatively great and irregular changes especially in industrial locations. A change of 0.01 per cent in carbon dioxide content will ordinarily produce a substantial change in indication. Control of atmospheres may be practiced in other ways than by using a transparent substantially closed container as herein described.

In the manufacture of lead-calcium cable sheath as known to us to have been practiced to date only virgin "chemical" lead has been employed. This grade of lead is substantially free from As, Sn, Bi, Fe, Sb and Zn, and contains about 0.004 per cent Ni, 0.06 per cent Cu and 0.007 per cent Ag. The variation in concentration of these elements in the supply of commercial lead of this type has not been found to be great enough to cause substantial interference with the indications given by the casting test. However, the method is influenced by certain variations in impurity content which are in excess of those normally encountered in the usual supply. The presence of tin to the extent of a few thousandths of one per cent causes low indications of calcium content. The use of high purity lead in place of "chemical" lead has a similar effect. Bismuth additions up to 0.1 per cent are inconsequential. Arsenic and antimony form compounds with calcium which drop off in the mixing kettle so that these elements would not be found in the finished sheath. Correction can be made for the effects of the interfering impurities referred to above, when their presence is known, by varying the atmosphere in the casting chamber, by admixture with a known proportion of alloy having a predetermined higher calcium content, or by a special set of test pieces of known calcium content and having the impurity to the same extent as the material to be controlled. By these procedures fissuring can be made to occur in alloys that otherwise do not give this manifestation. In factory operation those in charge know or can determine the brand

of lead that is being used and be enabled to make the necessary adjustments in the conditions of the test to compensate for the particular impurities and amounts thereof which are present.

Sufficient data have been collected in both laboratory and plant practice to establish that the method here presented is rapid, reliable, and helpful for plant control application. It is also adequately exact. From a broad aspect the use of atmospheres in accordance with the invention is not limited to the use of atmospheres containing only the usual constituents of the earth's atmosphere; these may be employed in proportions widely different than in any atmosphere commonly found in the open or in buildings; moreover, the presence of other artificially introduced gases is not excluded, when these affect the surface according to their proportion their proportion is controlled, carbon tetrachloride is an example of such a substance which has been found to affect the surface appearance but the control of which per se without controlling other constituents has not been found to be an accurate indicator for analytical purposes.

As stated, tin affects the results, hence with the use of known amounts of compositions of known calcium content as addition agents the method can serve for the control of tin content or detection of excess tin content in lead used in factory operations.

What is claimed is:

1. The method of determining quantitatively the constituents of a metallic alloy of the type wherein variations of one constituent result in significant changes in the exposed surface of samples of the alloy with various ranges of said constituent when cast under an atmosphere of known and definite composition, which comprises, first casting a standard series of samples of alloys containing known different amounts of the one constituent under said definite known atmosphere, and casting a sample of the alloy, of which the amount of said one constituent is to be determined, under an identical atmosphere and under similar conditions and arranging said sample and said standards for comparison of its exposed surface with the exposed surfaces of the standard series of sample.

2. The method of determining the calcium content of a lead-calcium alloy which comprises casting the alloy in a definite atmosphere containing constituents which act upon the surface of the alloy during cooling and arranging said casting for comparison of the surface thereof with the surfaces of castings of lead-calcium alloy having known calcium content determined in another manner which are cast in a substantially identical atmosphere whereby the calcium content of the casting may be determined.

3. The method of maintaining substantially at a single desired value the calcium content of calcium-lead alloy articles which comprises taking samples from different molten batches of said alloy, casting said samples under an atmosphere having the same fixed and known water vapor and carbon dioxide content, and altering the lead-calcium ratio in a batch that differs in its surface characteristics from such characteristics of a casting made under such an atmosphere and having the desired calcium content to produce an alloy of the desired calcium content.

4. In the method of manufacturing a product comprising a lead-calcium alloy in which the ratio of calcium to lead is maintained at a sub-

stantially constant value, the steps of taking successive samples of the molten alloy as it is produced and before it is used to make said product, casting said samples under a fixed and constant artificial atmosphere of known water vapor and carbon dioxide content, and changing the relative amount of one of the metallic constituents of the alloy when the surface characteristics of a cast sample differ from the surface characteristics of the alloy of said constant ratio cast under the same atmosphere.

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