A Rapid Visual Test for the Quantitative Determination of Small Concentrations of Calcium in Lead*

By EARLE E. SCHUMACHER and G. M. BOUTON

A method is described for estimating calcium in lead which consists in casting a test ingot in a prescribed manner and comparing its surface appearance with the surface appearance of standards. The calcium content can be determined by inspection.

IN THE manufacture of lead-calcium sheath it is desirable to control the calcium content to $0.028 \pm .005$ per cent in order to obtain the most desirable combination of properties. Since calcium is a very active element chemically, special manufacturing procedures were 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 not entirely satisfactory 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 melting kettle control. Quantitative spectrographic analysis methods were carefully tested, and while they showed some advantage over conventional methods, they were still unduly time consuming.

With the ever increasing interest in lead-calcium alloys for cable sheath, storage-battery grids, and other applications, it became desirable that a rapid, reliable and not too costly method be developed for determining their calcium content. In approaching the problem, several methods of attack involving physical, chemical, or electrical properties suggested themselves. A few of the methods investigated were:

1. Observations of the rate of oxidation or tarnish of freshly cut surfaces using a variety of atmospheres and temperatures.
2. Thermal EMF measurements against pure lead.
3. Measurements of hardness or strength of samples after various heat treatments.
4. Measurements of electrode potentials in various solutions.
5. Use of various metallographic techniques.
6. Observation of recrystallization tendencies after the samples had been deformed.

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Unfortunately, none of these methods proved adequate. Either the properties involved were insufficiently sensitive to changes in calcium content, or other factors masked the effect of calcium.

Early in the study of lead-calcium it was noticed that the molten alloys quickly filmed over with oxide. Careful 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. However, when these alloys were chill cast with as little agitation as possible, the surface of the ingots became progressively duller with increasing calcium content to a certain value. Further increase in calcium content resulted in the fissuring of the surface oxide leaving bright metallic areas exposed. This fissuring phenomenon, which is illustrated in Fig. 1, is the type of composition-sensitive indicator desired. When samples of lead-calcium are melted and cast under controlled conditions the surface markings 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. For clearness of illustration the samples were photographed under lighting conditions that made the bright highly reflecting surfaces appear dark in the photograph.

The success of the method is dependent to a large extent on the details of procedure that are given below. Since calcium is readily removed from lead by oxidation, a melting and casting procedure for the test specimens was adopted that resulted in a minimum loss of calcium. Fluxes and inert atmospheres, which normally provide adequate protection against oxidation, could not be used here since they seriously interfere with the fissuring phenomenon that is the basis of the method. The means finally adopted consists in melting a strip of the cable sheath to be tested in a hemispherical sheet iron crucible about two inches in diameter. A Bunsen burner flame of sufficient intensity to melt a 100-gram sample in about two minutes is applied to the bottom of 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 slight modifications in technique, samples for analysis may be taken directly from the commercial melting kettles. The mold used is probably

Per Cent Calcium

.021 .024 .026 .028 .030

Fig. 1—Surface appearance of test ingots of chemical lead-calcium alloys cast in atmosphere containing 0.02% carbon dioxide and having 50% relative humidity. The dark areas are very bright when viewed with directly reflected light. Approximately full size

not critical in shape or size.   The one used in this development is an iron plate $\frac{3}{4}$ in. x 4 in. x 8 in. with a tapered depression milled in its surface. The test ingot is about 4 in. long, $\frac{5}{8}$ in. wide, $\frac{1}{32}$ in. thick at the casting end and $\frac{3}{8}$ in. thick at the other end.   It weighs 80 to 100 grams.   The effect of mold temperature has been studied and is not 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.

Control of the atmosphere over the surface has been found necessary to insure reproducible results.   For this reason the cellophane enclosed casting chamber shown in Fig. 2 was devised.   There is a door on the right hand side for insertion of the crucible and a rubber inlet tube on the left for entry of the gas mixture.   It has been found by experiment that both moisture and the carbon dioxide content of the air influence the results obtained.   Therefore, both are removed chemically and then re-introduced
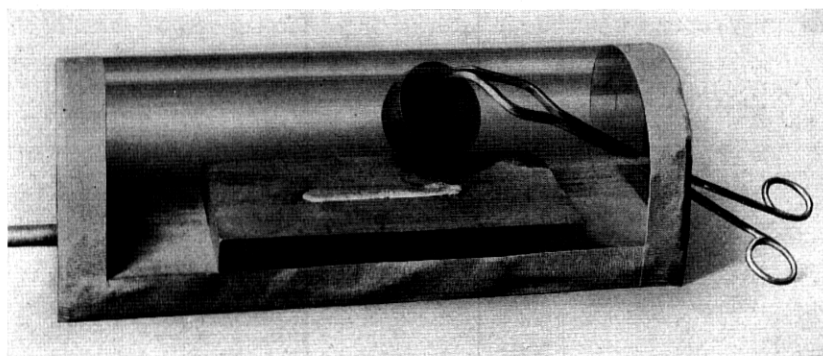

Fig. 2—Apparatus used in casting lead-calcium ingots under controlled atmospheres

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 certain salt 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 CO_2 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 shown in Fig. 3.

The surface appearances shown in Fig. 1 were obtained by casting in an atmosphere having 50 per cent relative humidity and 0.02 per cent carbon dioxide.   Increasing the carbon dioxide or decreasing the moisture content

causes the surfaces to become brighter 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. Alloys having calcium contents 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.

To date most experience with the use of the visual test for calcium has been on alloys made with chemical lead. 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 commercial supply has not been found to be great enough to cause serious 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
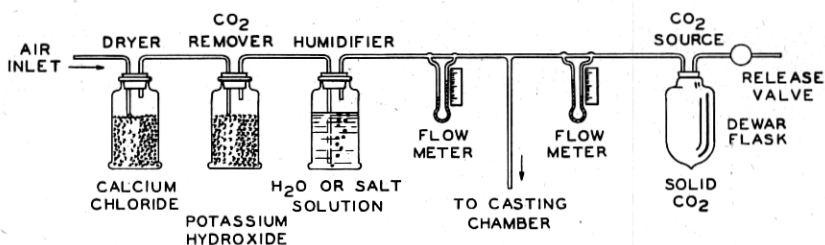

Fig. 3—Apparatus used for regulating atmosphere composition

usual supply. The presence of tin in the order 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 dross off in the mixing kettle so that these elements would not be found in the finished sheath. The effects of the interfering impurities referred to above can be corrected for, when their presence is known, by varying the atmosphere in the casting chamber or by admixture with a known proportion of alloy having a pre-determined higher calcium content. By these procedures fissuring can be made to occur in alloys that otherwise do not give this manifestation. In practical operation the brand of lead being used will be known and the necessary adjustments can be made in the conditions of the test.

Sufficient analytical data have been collected to establish the fact that the method here presented is rapid, reliable, and extremely helpful for plant control application.