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SUBDIVIDED LEAD PRODUCT

Albert P. Giraitis, James D. Johnston, and Hymin Shapiro, Baton Rouge, La., assignors to Ethyl Corporation, New York, N.Y., a corporation of Virginia

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This invention relates to subdivided metal. More particularly, the invention relates to a new form and composition of essentially lead metal particles, and to low creep—high strength stock shapes therefrom.

The highly desirable chemical properties of lead metal have been known for many years, with respect to resistance to corrosion, inactivity, ease of working, and general inertness. Accordingly, it would be expected that lead metal would find extremely wide usage for many process and building purposes. This has been true to a certain extent, but certain physical properties of lead mitigate against its utilization for many purposes. Principal disadvantages of lead metal in this respect are the relatively low tensile strength and tendency of the lead metal to experience plastic flow or "creep" during an extended period of service under even modest stresses. Accordingly, very few applications of lead have been evolved in which any degree of mechanical strength is necessary. The equipment and building usage of lead, then, have been mostly restricted to instances in which the lead metal is firmly attached or supported by a more reliable material, or the lead has been alloyed with other components present in substantial concentration. Accordingly, a significant need has long existed for a technique or composition which would retain the highly desirable chemical properties of lead, as a material of construction, but which would avoid the severe weaknesses heretofore encountered.

The present inventon has as its principal object, then, providing a new form of lead metal which is capable of fabrication to articles which retain the chemical desirable features of lead metal, but also possess vastly improved mechanical properties. An additional object is to provide a method for preparation of this new lead material. Yet another object is to provide a new composition or article comprising finely subdivided, predominantly lead particles susceptible of fabrication into gross articles of significantly superior mechanical properties, and for other purposes. A further object is to provide lead in the form of new and improved stock shapes having greater mechanical strength than heretofore available. Other objects will appear hereinafter.

The present invention comprises subdivided, predominantly lead particles, which are characterized by being essentially lead metal, but in the form of irregular small particles having significantly higher surface characteristics than any material heretofore provided, actually being a porous material. By this is meant that the individual particles or fragments have a spongy or permeated surface characterized by a large number of interstices leading to the interior of each particle. In addition, the particles appear to be entirely amorphous, that is, no definite crystalline appearance is exhibited, some of the particles actually resembling popcorn in magnified appearance.

In addition to the existence of the channels, pores, or interstices to the interior of each particle of the subdivided lead material, the product of this invention is further characterized by the virtual freedom from or absence of any organometallic component of lead. It is found that the presence of organolead compounds, of a normally liquid nature, above approximately 0.2 weight percent have a strong tendency to weaken ultimate shapes fabricated from the powders. Thus, it is highly preferred that the powder be purified to the extent of having no more than about 50 parts per million (0.005 weight percent) of such a component present. Even more desirable, it is preferred that the concentration should not exceed about 15 parts per million. However, a minute quantity of inorganic compounds, and in particular inorganic compounds of lead, particularly the chloride and the carbonate, are provided on the surface of the particles. By surface is meant not only the obvious external surface of the discrete particle, but the aforementioned pores or channels. Although the presence of inorganic lead compounds is tolerated, and is beneficial in limits, yet the quantity thereof is usually so low as to be relatively inconsequential. The chemical composition of the particles is usually at least about 98 and, frequently, above 99.5 weight percent free and uncombined lead. Similar limits on the presence of water are also preserved. The presence of even small amounts of water as an impurity results in a reduction of the strength of the cold worked shapes, so that the moisture content is reduced to below about two percent, and preferably below about 0.1 weight percent.

Another significant attribute of the present product is the size range and distribution of the particles. It is found that a screen analysis, using a standard series of screens (U.S. sieve series, Chemical Engineer's Handbook, McGraw-Hill, 1934, pp. 1448) shows a straight line distribution when plotted as cumulative percent retained versus screen openings on log-log graph paper. Further, substantially all the particles pass through a No. 10 screen (having opening dimensions of 0.0787 inch), and at least about two-thirds is retained on a No. 200 screen (having opening dimensions of 0.0029 inch). More particularly, in practically all cases, from 70 to 95 percent of the product is retained on a 200 mesh screen.

Over and above the indicated range of sizes, it is further found that a particular fraction, minus extremely fine and the more coarse fraction is found greatly superior to random distribution within the indicated broad range. As will be clear hereinafter a fraction retained on a No. 325 screen and passing a No. 100 screen, exhibits greatly superior properties. In other words, a preferred range is particles passing screen openings of 0.0059 inch and retained on a screen with openings of 0.0017 inch. It will be understood that the foregoing screen opening dimensions will correspond generally to the controlling dimensions of individual particles in screening.

The product of the present invention is made by reacting an alloy, of lead with a reactive metal, especially an alkaline or an alkali metal, such as sodium, with a reagent capable of reacting with the said electropositive metal component and with the lead of such an alloy. By the above requirement is meant that the chemical reagent reacts both with the electropositive metal component from the feed alloy, and jointly reacts with part of the lead metal. A typical reaction suitable as the initial step of the preparatory process involves the reaction of monosodium lead alloy with ethyl chloride, which results in the formation of sodium chloride, tetraethyllead, and lead metal, the lead metal comprising at least three-fourths of the lead component of the alloy initially charged. Upon completion of such a reaction, a reaction mixture comprising sodium chloride, tetraethyllead, lead metal, and minor quantities of unreacted alloy is available. This is then further treated, typically as follows: first the reaction mixture is contacted with water which reacts with any free alkali metal unreacted and converts it into a soluble alkali metal hydroxide. A distillation operation is provided to separate the major portion of the organolead formed during the reaction, leaving an aqueous slurry of sodium chloride largely dissolved in water, lead metal, and only minor quantities of residual ethyl chloride. In addition, the distillation above described

does not remove all of the tetraethyllead, but a significant quantity is retained in the system, probably because of the high surface characteristics which are engendered by the reaction and are essential in the ultimate product. The subsequent processing includes further contacting of the lead solids with water, which removes additional sodium chloride. This is followed by free draining of a sludge from this treatment. By free draining is meant that excess liquid is merely drained from a perforated container holding the mixture, or by resting the mixture on an inclined plate until surplus liquid drains away. The free drained sludge is then subjected to a thermal drying, plus a partial pressure operation, which lowers the residual organolead content to below about 25 parts per million of the resultant dry solids. The drying is carried out by subjecting the free drained sludge to heating for a relatively extended period at a temperature terminating at at least 100° C. and normally, in conjunction with the passage of an inert, non-oxidizing gas over and through the solids. This operation is resultant of the desired lead product of the present invention.

The lead solids thus produced exhibit the properties heretofore described, and when subjected to sufficient mechanical pressure and cold working, form solid shapes which exhibit tensile strength, stiffness, and retention of dimensional stability with time, far superior to the comparable properties when comparable shapes are established from other types of subdivided lead, or from melted lead.

The details of operation of a typical embodiment of the preparatory method of the present invention are described below. All parts or concentrations herein are in parts by weight, except as otherwise stated.

Example I

100 parts of sodium lead alloy were charged to an autoclave along with about 50 pounds of ethyl chloride, this amounting to approximately 75 percent excess ethyl chloride. The mixture was reacted under autogenous pressure at elevated temperature, until reaction is terminated as shown by a decrease in temperature and pressure. The product of this reaction was an apparently dry reaction mass containing about 55 weight percent lead, 24 percent tetraethyllead, and 20 percent sodium chloride. Excess ethyl chloride was vented during the reaction and upon completion of the reaction. The dry granular material was then discharged from the autoclave and immersed in water, then was subjected to steam distillation for a sufficient period of time to remove a large proportion of the tetraethyllead component. The resultant material is a multi-phase mixture of the subdivided lead particles, sodium chloride (largely dissolved in the aqueous phase) and minor quantities, of the order of perhaps several percent, based upon the lead, of tetraylthyllead. This mixture was then discharged from the distillation vessel, and contacted with additional water for a variable period of time, or from about one hour to 24 hours, although this is not a significant factor in preparation.

The mixture was then free drained, that is, merely lifted from the retention vessel to which it is charged after the steam distillation, and was then subjected to an additional drying operation. This was carried out at a temperature of about 180° C. for about 2 hours and with passage of a stream of nitrogen through the mass being dried. As a result of this treatment, the tetraethyllead content was reduced to below about 15 parts per million based upon the lead content, with a comparable reduction in the water content. The sodium chloride and inorganic lead content are similarly quite low.

After cooling of the so-formed powder to ambient temperatures, the material was ready for further mechanical processing as described hereinafter. The solids, upon microscopic examination appear to be rounded edge granular agglomerates having an obviously porous surface, but apparently a homogeneous composition. In other words, substantially all the non-lead metal components present are associated with the individual particles of the product.

Screening of this material in U.S. Standard screens gives the following size distribution:

Cumulative percent retained	Screen No.	Dimension of screen openings (inches)
9	18	0.0394
15	25	0.0280
25	35	0.0197
36	45	0.0138
57	100	0.0059
73	120	0.0049
84	200	0.0029
97	325	0.0017

Portions of the above described material are pressed into blanks of about one-eighth inch thickness, by distributing in a form and applying a pressure of from about 1 to 5 tons per square inch. A shape or blank of more or less fragile nature is thus produced. This blank is then subjected to a rolling operation, providing a further size reduction to a thickness of about 1/32 inch, or a volume reduction of about 1:4. The thin plate resulting has a relatively high gloss surface and exhibits great stiffness, entirely unlike massive lead.

Determination of the tensile strength of a plate, made from the product having the size distribution as given heretofore, showed a tensile strength of about 5,500 pounds per square inch. This is greatly superior to the tensile strength of only about 2,000 p.s.i. for pure lead, and also is greatly in excess of a strength of 4,000 for hard lead, or antimonial lead.

As heretofore mentioned, a preferred size fraction is the fraction passing a No. 100 screen and retained on a No. 325 screen, as shown by the results of the following example.

Example II

The preparatory method of Example I was repeated, but the product was screened to separate a portion retained on a No. 325 screen and passing a No. 100 screen. In other words, the particles ranged from 0.0017 to about 0.006 inch in size. Processing of this fraction as in the preceding example gives a sheet having an ultimate tensile strength of about 7,500 pounds per square inch.

To further illustrate the surprising benefits achieved from the present product, comparable fabrication of mechanical comminuted lead specimens were carried out. When processing a lead wool, plates or sheets were obtained having a tensile strength of only about 2,500–2,600 pounds per square inch. When somewhat spherical particles, produced by melting lead and atomizing the molten metal, were processed, the maximum ultimate tensile strength averaged about 3,800 pounds per square inch. It is thus seen that the present product provides exceptionally superior strength. Further, the creep tendency of stock sheets produced as in Examples I and II is of the order of a small fraction of a percent per year, under moderate working stresses.

Although monosodium lead alloy NaPb having 10 weight percent sodium is the preferred starting material to make the product of the present invention, other alloys, and in particular, alloys having compositions corresponding to chemical compounds, are highly suitable, as in the following example.

Example III

In this operation, the starting material is a sodium lead alloy containing approximately 20 weight percent lead, this corresponding to the formula Na_9Pb_4. The lead particles resultant after reaction, separation of the tetraethyllead and further drying as in the preceding operations, exhibits corresponding properties when mechanically processed.

Although the alkali metal alloys of lead are the more usual and convenient starting materials, the alloys of lead with magnesium, zinc and calcium are also suitable. In all cases, a reagent is employed which converts a portion of the lead to an organometallic, although, as already noted, the final product is denuded of such components. The alloy compositions found most desirable are those which are actually single compounds, as in the examples given. However, this condition is not absolutely essential—for example, a sodium-lead alloy having 15 percent sodium can be used quite effectively.

Alkyl chlorides are the preferred treating agents for the initial step in preparing the lead powders, but, other alkyl halides can be employed. Similarly, it is not essential that the alkyl group be the ethyl group, but other lower alkyl halides are suitable, for example, isopropyl chloride, n-butyl chloride, methyl chloride and the like. When these materials are substituted for the ethyl chloride used in the preceding examples, and similar treatment is given to solids, comparable results are provided.

The preparatory method for the present product is susceptible to substantial variation, as long as the principles outlined above are generally followed. It appears that the reason for the efficacy and unusual properties of the lead powder of the present invention lies in the fact that a homogeneous alloy is initially reacted with a reagent which is susceptible or capable of reacting with the non-lead alloy component and with the lead itself to a certain extent. It is believed that the reaction can be analogized to the physical leaching of alloying metal from the alloy, plus, of course, the partial reaction of some of the lead present. Following the reaction, in every case, subsequent treatment to substantially completely separate inorganic metal salts and organometallic lead compounds from the reaction mixture is necessary, supplemented with a high effectiveness drying operation. It is found that even minor quantities of organometallic materials left in the lead would result in a great decrease in the tensile strength of the lead. In addition to the virtually complete removal of the organolead compound, under non-oxidizing conditions, the degree of removal of combined lead and extraneous metal compounds is quite important. A high degree of removal of non-metallic components is highly desirable, but on the other hand, miinute traces or trace quantities of compounds are found to contribute to the mechanical strength of the formed stock shapes produced from the lead powder. These components are principally minute proportions of alkali metal chlorides (as in the preceding examples, wherein a sodium lead alloy was used along with an alkyl chloride reactant) and a lead oxide-lead carbonate complex material. Lead halide and lead oxide components can also be present as impurities. The presence of up to about 1.5 percent of such compounds contributes to the strength of the ultimate cold worked stock shapes.

The true basis or reason for the strength and finish of stocks made from the lead powder of this invention is not completely understood. Although the product is apparently amorphous particles, it is believed that these are, in fact, actually agglomerates of crystalline lead, wherein the crystals are, in fact, so small as to be considered macro-molecular. Accordingly, in the ultimate stock shapes, the crystal boundaries are many times the magnitude of the crystal boundaries in conventional lead shapes. Hence, a significant proportion of the strength arises from the physical configuration of the lead particles proper. As already noted, the minor quantities of impurities, especially alkali metal halides and certain lead inorganic compounds, also contribute to the ultimate tensile strength. The reason for this supplemental benefit is not fully established. However, as in the case of the lead metal, the impurities are believed to exist as macro-molecular entities intimately associated with the extremely fine lead crystals comprising the lead component of the powder. In the cold worked stock shapes

then, such compounds are present as compound crystals interrupting inter crystalline contact of the lead crystals. This, in effect, appears to increase the resistance to crystal or grain face slippage, which occurs in deformation, thus increasing strength.

The utility of the powder from the present invention is not limited to formation of cold worked stock pieces, but extends to the formation of composite or polymetallic articles. Thus, it is found that the powder can be applied to a base metal component and rolled thereon in such a manner that a strong, adherent coating of high strength lead is applied. Thus, for a relatively light weight roof shingle, a ferrous metal base member can be coated with the powder of Example I or Example II, and a rolling pressure of the order of 20,000 to 50,000 pounds per square inch can be applied resulting in a mechanical adherent plating of this member. Since the lead coating in such instances can be of the order of $\frac{1}{64}$ of an inch thick, it is apparent that a roofing material is thus generated having the superior properties of lead with none of the weight disadvantages.

It will be readily apparent that numerous other stock shapes are readily produced from the product, in addition to the thin plates illustrated by the examples. When comparable techniques are employed to make bars, channels, strips, or rods, the stock shapes resultant exhibit comparable stiffness, surface finish, and ultimate tensile strength. Suitable construction purposes for such shapes are as window mullions, gutters, or preformed roof flashing members.

The techniques of cold working the powders to desired stock shapes are many and varied. By cold working is meant that the forming operations carried out on the subdivided lead are at a temperature below the melting point of lead. Ordinarily the work input to the material results in a temperature increase, but, in practically all instances, temperatures of below 200° C., and preferably not over 150° C., are provided.

The preferred type of cold working operation, as clear from the examples above involves a final rolling operation characterized by a moderate angle of nip. It is difficult to define precisely the actual unit pressure applied in such an operation, but it appears to be of the order of 20,000 to 100,000 pounds per square inch. The greater the degree of volume reduction, the greater the pressure required. Batch processing can be employed, or, if desired, continuous processing through several stands of rolls can be used. In such instances, the first stand of rolls usually apply only sufficient pressure to provide enough cohesion, of the rough work piece so formed, so that it feeds smoothly to the subsequent working rolls.

What is claimed is:

1. An essentially lead powder, the particles thereof being amorphous irregular shapes and having channels or pores admitting to the interior of said particles, and from 70 to 95 weight percent of the powder being retained on a No. 200 U.S. screen, the powder having a lead content of at least about 98 percent and up to 1.5 weight percent impurities, said impurities being selected from the class consisting of lead chloride, lead carbonate, alkali metal chloride and lead oxide, and being essentially free of organometallic lead compounds, said lead powder having been produced by reacting an alkali metal-lead alloy with an alkyl chloride to form a product mixture including unreacted lead and an alkyllead compound, then separating from the product mixture, in the presence of an aqueous phase, a substantially lead powder fraction, then drying said lead powder at a temperature below the melting point of the lead and above about 100° C., and in the presence of a non-oxidizing gas for a sufficient time to free the lead powder of alkyllead residues, and thereafter screening the so-dried lead powder.

2. A lead powder as defined in claim 1, further defined in that substantially all the particles are retained on a

No. 325 U.S. screen and passed through a No. 100 U.S. screen.

3. A cold formed essentially lead stock having high gloss surface and a tensile strength above 5,000 pounds per square inch, said stock being formed by subjecting a lead powder as hereinafter defined to cold working pressure of at least about 25,000 pounds per square inch, said powder consisting of particles having amorphous irregular shapes and having channels or pores admitting to the interior of said particles, and from 70 to 95 weight percent of the powder being retained on a No. 200 U.S. screen, the powder having a lead content of at least about 98 percent and up to 1.5 percent impurities, said impurities being selected from the class consisting of lead chloride, lead carbonate, alkali metal chloride and lead oxide, and being essentially free of organometallic lead compounds, said lead powder having been produced by reacting an alkali metal-lead alloy with an alkyl chloride to form a

product mixture including unreacted lead and an alkyllead compound, then separating from the product mixture, in the presence of an aqueous phase, a substantially lead powder fraction, then drying said lead powder at a temperature below the melting point of the lead and above about 100° C., and in the presence of a non-oxidizing gas for a sufficient time to free the lead powder of alkyllead residues, and thereafter screening the so-dried lead powder.

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