United States Patent Office

3,320,664

Patented May 23, 1967

3,320,664

PROCESS FOR THE PRODUCTION OF DISPERSION STRENGTHENED LEAD

Tibor Krantz, Fort Saskatchewan, Alberta, David John Ivor Evans, Edmonton, Alberta, and John Alfred Heath Lund, Vancouver, British Columbia, Canada, assignors, by mesne assignments, to St. Joseph Lead Company, a company of New York

No Drawing. Filed Apr. 19, 1965, Ser. No. 449,275
Claims priority, application Canada, Apr. 26, 1962, 847,599
12 Claims. (Cl. 29—420.5)

This is a continuation-in-part application of Ser. No. 202,053, filed June 13, 1962, now abandoned.

This invention relates to a process for the production of dispersion strengthened lead. It is particularly directed to providing a process for the production of lead which is of high tensile strength and which possesses a high resistance to creep.

Pure lead possesses, for many uses, natural advantages over other metals due to its ductility, its density, its resistance to corrosion and other well known physical and chemical properties. As a result, lead is selected over other metals for many structural uses, such as in piping, linings for reactors and reaction vessels, for sound proofing, protection against radioactive radiation, and the like. However, pure lead has several important disadvantages in that it is of relatively low tensile strength, of the order, for example, of only from about 2,500 to about 2,900 pounds per square inch at ambient temperature, and of low yield strength. Thus, lead metal, when used for structural purposes, usually requires reinforcement, stiffening or the support of stronger structural materials to provide the structural strength necessary for its intended purpose.

It is known that the tensile strength and hardness of lead can be increased by alloying it with other metals such as antimony, cadmium, calcium, tin and bismuth. However, the use of conventional alloying agents may detract from other desirable characteristics of the lead, particularly its chemical and electrical properties.

The tensile strength of lead can be increased by the addition of dispersoids, such as finely divided particles of alumina, lead oxide, magnesium oxide, calcium oxide, nickel and other additives. Such additives are provided in the lead such as by mixing or blending finely divided particles of the additive in the desired amount with finely divided particles of lead. The mixture of dispersoid and lead is then compacted into desired shape by known methods, such as by extrusion, roll compacting and stamping. We have found that while the addition of a dispersoid serves to increase the tensile strength of the lead, it is very difficult, if not impossible, to obtain distribution of a finely comminuted, hard, solid phase uniformly throughout the lead matrix due to agglomeration or seggregation if the dispersoid is mixed with the lead in the solid state, or agglomeration, segregation or volatilization if it is added to a molten bath of the lead. Thus, the dispersoid tends to be distributed non-uniformly throughout the matrix and, as a result, the product may not have uniform physical and chemical properties throughout.

We have found that dispersion strengthened lead, in which the dispersed phase is uniformly distributed and which is of high tensile strength, and of high resistance to creep, can be produced without adversely affecting normal physical and chemical properties inherent in refined lead, with the exception of a reduction in its normal ductility, by forming, in situ, on the surfaces of finely divided lead particles, a film or coating of a predetermined amount of lead oxide, and thereafter breaking the lead

oxide films into finely divided particles and dispersing them in a lead matrix.

The method of producing dispersion strengthened lead of this invention comprised, in general, the steps of moistening the surfaces of finely divided lead particles with water, mixing the moistened lead particles while exposed to a free oxygen containing gas, continuing the mixing step to form a film or coating of lead oxide on the surfaces of the individual particles, and thereafter breaking the soformed lead oxide film into finely divided particles and dispersing them in a lead matrix.

While the process of this invention can be simply stated, there are important factors which affect the physical and chemical properties of the resulting product. Such factors include, but are not necessarily limited to, the sizes of the individual lead particles, the amount of water used to moisten the lead particles, the temperature of the free oxygen bearing gas to which the lead particles are exposed, and the techniques used to form the powdered lead into useful products.

It is preferred to form relatively thin coatings of lead oxide on the surfaces of the comminuted lead particles. These thin lead oxide coatings are more easily comminuted into finely divided lead oxide particles and dispersed uniformly through the lead matrix by plastic deformation accompanying the formation of the oxidized lead particles into useful shapes.

In coating larger lead particles, it is necessary to form thicker lead oxide films on surfaces of the particles to obtain the same lead oxide content in the product which is obtained with thinner coatings on smaller particles due to the smaller surface areas of the larger particles exposed to the coatings. When the thick films break down during plastic deformation, the lead oxide is present as larger pieces and may not be distributed uniformly throughout the mass. Thus, the highest yield and tensile strengths are obtained in the final product when finely divided lead particles are used as the starting material. We have found that optimum tensile and yield strengths of the resulting product are obtained when particles are used of a size up to about 150 microns. Maximum strengths are obtained when the particles are smaller than about 10 microns.

It is realized that the terms "thin" and "thick" as used herein are relative. It is difficult to obtain direct measurements of the thickness of the films. However, it is possible to calculate the thickness of the oxide coating on a particle having a specific oxide content. For example, the coating on a fine, 7 micron, lead particle which contains 20% lead oxide is calculated as of 0.3 micron thick. A coating on a coarse, 35 micron, particle which contains 10% lead oxide is calculated at 0.8 micron thick.

We have found that the mixing step should be conducted in the presence of a free oxygen containing gas, such as air, at a temperature below about 100° C. and preferably at about ambient temperature, for example, from about 15° to about 30° C. When the oxidation step is conducted at an elevated temperature, from above about 100° C. to about 327° C., the melting point of lead, it is difficult to control the rate of oxidation and the degree of oxidation is not uniform throughout the mass of the particles. Oxidation of dry particles at a temperature below 100° C. proceeds relatively slowly and is not necessarily uniform throughout the mass. However, if the particles are moistened with water, oxidation proceeds rapidly at ambient temperatures and can be controlled readily by the moisture content to produce a desired percentage of lead oxide within very narrow limits.

The degree of oxidation of lead to lead oxide with a specific water addition is directly related to the size of the lead particles. The finer the particles, the greater is the surface area exposed to the reaction and the greater is the total amount of oxide produced by the addition of a specific amount of water. We have produced, for example, refined lead particles which contain from a finite amount to 16% lead oxide, calculated in terms of PbO, by moistening refined lead particles of a size smaller than 10 microns with from 0.25% to 2% water and mixing them, in a conventional blender, for periods of 30 minutes. The degree of surface oxidation of the particles can be controlled closely by controlling the moisture added to the particles.

The amount of water used may be varied over a wide range, from about 0.05% up to 2% or more and the surface oxidation of the particles may amount to from about 1% to about 15% calculated as PbO. In general, a surface oxide coating in the range of from about 2% to about 10% is particularly useful. The water may be introduced into the blending operation as liquid water in the form of a spray or mist or in a current of air containing water vapor in such amounts that its dew point is higher than the temperature of the lead particles in the blending apparatus.

Moistening and mixing, or blending, can be conducted as a single operation. Conventional apparatus for mixing solids are well known and are widely used. Such apparatus includes rotating pans with offset blades, helical ribbon mixers, tumbling barrel mixers, rake mixers, double cone mixers and the like. A double cone mixer was used with very satisfactory results. The prescribed amounts of water and refined lead particles were charged into the water and mixed for predetermined time periods.

The lead oxide coatings formed on the surfaces of the lead particles are comminuted, or broken down, into finely divided particles and dispersed uniformly throughout the lead matrix by plastic deformation, such as, for example, by explosive forming, die stamping, extrusion, and roll compacting. The plastic deformation step may be conducted to produce a finished commercial product, such as tubes, pipes, lead strip or sheet, or other desired shape or it may be conducted to produce an intermediate shape such as a billet which can be worked to produce a desired product.

The following examples illustrate the operation of the process of this invention and the physical characteristics of the dispersion strengthened lead produced thereby. Throughout the example, the terms "fine," "medium," and "coarse" particles are used to designate particles of sizes smaller than 10 microns, from 10 to 50 microns, and larger than 50 microns respectively. The amount of lead oxide contained in each sample was determined by measuring the weight loss after heating the sample of the treated lead particles at 315° C. for 30 minutes in an atmosphere of hydrogen. The amount of lead oxide present in the samples was calculated in terms of PbO.

The term "lead oxide" used throughout the description of the invention and in the claims in referring qualitatively to the lead oxide present in the lead is intended to include any and all oxides of lead which are produced, as the improved physical properties of the treated lead are obtained regardless of the specific oxide or oxides of lead which may be formed in the operation of the process. However, X-ray diffraction studies indicate that at least the major portion of the oxides formed by the method of the invention is PbO.

Example 1

1,000 grams of refined, fine lead powder which originally contained 2.6% lead oxide, calculated as PbO, was spread in a thin layer on a tray. Air at ambient temperature, about 29° C. was circulated through the layer. At the end of 24 hours, the particles were found to contain 3.25% lead oxide as PbO. At the end of 94 hours exposure, they contained 3.35% lead oxide as PbO.

Example 2

Three samples of the same type powder as used in Example 1 were mixed, in air, with 0.5, 1.0, and 2.0%, by weight, water by blending in a double cone blender for 30 minutes. The samples were then exposed to the atmosphere by spreading them in thin layers on trays. The following Table 1 shows the lead oxide content, calculated as PbO, of the samples after 30 minutes blending and after exposure to the air for various time periods.

TABLE I

Water	Sample — Lead Oxide Content Calculated as PbO		
	After blending 30 minutes	After Air Exposure	
		22 hours	94 hours
0.5%	5.8	5.8	
1.0%	9.4		10.2
2.0%	16.0	16.1	

Example 1 illustrates that oxidation of the particles proceeds very slowly when air alone at ambient temperature is employed as the oxidizing agent. Example 2 illustrates that oxidation proceeds rapidly at ambient temperature when the particles are moistened with water and blended, or mixed, in air at ambient temperature.

The following Table 2 illustrates the ultimate tensile strength (UTS), yield strength (YS) and elongation (E) of lead products formed by plastic deformation of lead particles coated, in situ, with lead oxide by oxidation at ambient temperature, using varying amounts of water.

The lead oxide coatings are comminuted and dispersed throughout the lead matrix by compacting the oxidized powder into billets at a compacting pressure of 35 tons per square inch and then extruding them through a die having an opening 0.25 inch in diameter.

TABLE 2

Added Water	Lead Particle Properties	1	2	3	4
		Fisher Micron Size			
		35.6	8.5	8.0	62
0%	PbO	1.9	2.6	3.1	0.7
	Extrusion pressure, tons	51	61	62	42
	U.T.S., p.s.i.	4,360	5,660	5,850	3,200
	Y.S., p.s.i.	4,160	5,470	5,520	2,790
	E, percent	22	20	21	38
.25%	PbO	4.4		6.2	2.5
	Extrusion pressure, tons	58		74	44
	U.T.S., p.s.i.	5,000		6,790	3,400
	Y.S., p.s.i.	4,600		6,590	3,060
	E, percent	15		14	35
.50%	PbO	4.7	5.8	7.1	2.9
	Extrustion pressure, tons	58	65	60	53
	U.T.S., p.s.i.	5,020	6,230	6,970	3,380
	Y.S., p.s.i.	4,870	6,000	6,840	3,000
	E, percent	16	15	13	33
.75%	PbO	5.5		9.7	4.5
	Extrusion pressure, tons	62		63	56
	U.T.S., p.s.i.	4,920		7,460	3,380
	Y.S., p.s.i.	4,750		7,180	3,000
	E, percent	17		10	33

The strengthening effect of the lead oxide dispersed in the lead by the process of the present invention is readily apparent from the above table. This table also illustrates the effect of particle size on the strength properties of the lead products—the finest powder resulting in the strongest product.

The following Table 3 illustrates the effect of cumulative work conducted on a work sample produced by compacting and extruding lead particles oxidized, in situ, by the process of this invention. The work sample con-

tained 5% lead oxide and was extruded and re-extruded a total of eight times.

TABLE 3

Run No.	Extr. Pressure, tons	UTS, p.s.i.	YS, p.s.i.	Elong., percent
1	62	6,040	5,890	15.5
2	62	6,340	6,140	12.0
3	63	7,020	6,730	13.5
4	66	7,510	7,290	14.0
5	65	7,710	7,450	14.0
6	68	8,040	7,870	15.5
7	72	8,240	8,120	14.5
8	77	8,560	8,410	15.0

The results set out in Table 3 illustrate that both the ultimate tensile strength and the yield strength increase with increased work without appreciable reduction in the elongation.

The tensile strength of the lead product, for a specific oxide content, is found to be a function of the particle size of the lead powder. It is found, also, that the strength of the product is increased with increasing oxide content up to a certain maximum, which maximum also is dependent upon the particle size of the lead powder. For example, using a coarse, over 50 microns, powder, the tensile strength is found to increase linearily with an oxide content up to about 2.5%, calculated as PbO, and for a fine, smaller than 10 microns, powder it increases linearly to an oxide content up to about 4%, calculated as PbO. This may be explained by the observation that for a specific oxide content, the smaller the lead particles are, the thinner is the oxide layer; the greater are the number of oxide fragments produced during plastic deformation, for example extrusion; the smaller is the particle spacing in the compacted product, and the more uniform is the dispersion of the dispersoid or hard phase throughout the product. All these factors contribute to a higher strength product.

It has also been found that extrusions made from lead particles oxidized to a given oxide content in the presence of controlled amounts of water by the method of the invention show higher ultimate tensile strengths than those made from the same particles by oxidation with air at high temperatures. Samples from the same lot of lead powder oxidized to an oxide content about 3%, calculated as PbO, gave the following results:

Method	Percent PbO,	UTS, p.s.i.
Oxidized 2 hours in air at 350° F	3.5	6,507
	3.2	6,347
Blended 10 minutes with .08% H_2O at room temperature	3.2	7,730

Products formed of dispersion strengthened lead produced by the process of this invention possess many important advantages. Products were tested along their lengths and the maximum variations in ultimate tensile strength at different points along the length was found to be less than 2.5%, which is considered as uniform. A number of samples were aged for periods up to 4 months with only slight, but inconsistent, variations in the ultimate tensile strength and elongation values Aging appears to have no deleterious effect on the products.

Creep tests were conducted on samples using the cantilever beam loading technique. A refined lead product which contained 3.6% lead oxide, calculated as PbO, showed no evidence of creep under a load of 1,500 pounds per square inch. Further tests on samples which contained 3.1% lead oxide, calculated as PbO, and having an ultimate tensile strength of 6,200 pounds per square inch and an elongation value of 16.5% were tested for extended periods at temperatures of 30° C. and 85° C. with loads up to 1,000 pounds per square inch. None of the specimens showed detectable deformation in 17 day test periods under this load.

Samples of refined lead, 99.94% purity, and lead which contained 3.1% and 9.3%, respectively, of lead oxide, calculated as PbO, were subjected to corrosion tests in 10%, 50% and 85% sulphuric acid solutions at room temperature and in 10% and 50% sulphuric acid solutions at 90° C. The corrosion resistance of the lead-lead oxide samples was similar to, and in some instances slightly better than, that of pure lead.

Electrical resistivity measurements were carried out on samples which contained 3.6% lead oxide, calculated as PbO, and which were produced by extrusion followed by cold rolling to a thickness of 0.051 cm. The strip, which had an ultimate tensile strength of 6,430 pounds per square inch and an elongation of 12%, had an electrical resistivity of 22.9 microhms per centimetre, which compares very favorably with 20.65 microhms per centimeter of cast lead.

It is found, also, from hardness tests conducted on dispersion strengthened lead products produced by the process of this invention that the hardness remained stable at temperatures of from ambient temperature to 100° C.

The above tests illustrate that lead products produced by the process of this invention have high tensile and yield strength, high resistance to creep, reduced elongation and reduced ductility which do not interfere with the ability to work them by conventional plastic deformation methods, high hardness as compared with that of refined lead, without affecting, adversely, desired electrical and corrosion resistant properties.

It will be understood, of course, that modifications can be made in the preferred embodiment of the process described herein without departing from the scope of the invention defined by the appended claims.

We claim:

1. A method of making a high tensile strength lead product which comprises subjecting particles of metallic lead not exceeding about 150 microns in particle size to oxidizing conditions in the presence of controlled amounts of moisture to produce a coating of lead oxide thereon amounting to from about 1% to about 16% by weight calculated as PbO and thereafter subjecting a plurality of said particles to plastic deformation to comminute the so-formed lead oxide and disperse the comminuted lead oxide in the lead matrix formed by the adhesion of the oxide free surfaces of the particles.

2. The method defined in claim 1 wherein the particles of metallic lead do not exceed about 10 microns in particle size.

3. A method of making a high tensile strength lead which comprises moistening particles of metallic lead not exceeding about 150 microns in particle size with from about 0.05% to about 2% of water by weight, exposing the moistened particles to a free oxygen containing atmosphere to produce a coating of lead oxide thereon amounting to from about 1% to about 16% by weight calculated as PbO and thereafter subjecting a plurality of said particles to plastic deformation to comminute the so-formed lead oxide and disperse the comminuted lead oxide in the lead matrix formed by the adhesion of the oxide free surfaces of the particles.

4. A method of making a high tensile strength lead which comprises moistening particles of metallic lead not exceeding about 150 microns in particle size with from about 0.05% to about 2% of water by weight, stirring the moistened particles in a free oxygen containing atmosphere to produce a coating of lead oxide thereon amounting to from about 1% to about 16% by weight calculated as PbO and thereafter subjecting a plurality of said particles to plastic deformation to comminute the so-formed lead oxide and disperse the comminuted lead oxide in the lead matrix formed by the adhesion of the oxide free surfaces of the particles.

5. A method of making a high tensile strength lead which comprises moistening particles of metallic not

exceeding about 150 microns in particle size with from about 0.05% to about 2% of water by weight, stirring the moistened particles in a free oxygen containing atmosphere at a temperature below about 100° C. to produce a coating of lead oxide thereon amounting to from about 1% to about 16% by weight calculated as PbO and thereafter subjecting a plurality of said particles to plastic deformation to comminute the so-formed lead oxide and disperse the comminuted lead oxide in the lead matrix formed by the adhesion of the oxide free surfaces of the particles.

6. A method of making a high tensile strength lead which comprises moistening particles of metallic lead not exceeding about 10 microns in particle size with from about 0.05% to about 2% of water by weight, exposing the moistened particles to a free oxygen containing atmosphere to produce a coating of lead oxide thereon amounting to from about 1% to about 16% by weight calculated as PbO and thereafter subjecting a plurality of said particles to plastic deformation to comminute the so-formed lead oxide and disperse the comminuted lead oxide in the lead matrix formed by the adhesion of the oxide free surfaces of the particles.

7. A method of making a high tensile strength lead product which comprises subjecting particles of metallic lead not exceeding about 150 microns in particle size to oxidizing conditions in the presence of controlled amounts of moisture to produce a coating of lead oxide thereon amounting to from about 1% to about 16% by weight calculated as PbO and thereafter subjecting a plurality of said particles to extrusion to comminute the so-formed lead oxide and disperse the comminuted lead oxide in the lead matrix formed by the adhesion of the oxide free surfaces of the particles.

8. A method of making a high tensile strength lead product which comprises subjecting particles of metallic lead not exceeding about 150 microns in particle size to oxidizing conditions in the presence of controlled amounts of moisture to produce a coating of lead oxide thereon amounting to from about 1% to about 16% by weight calculated as PbO, forming a billet of said particles by compaction under pressure and extruding said billet.

9. Lead particles not exceeding about 150 microns in particle size having surfaces coated with lead oxide in an amount of from about 1% to about 16% by weight calculated as PbO.

10. Lead particles not exceeding about 10 microns in particle size having surfaces coated with lead oxide in an amount of from about 1% to about 16% by weight calculated as PbO.

11. A method for producing dispersion strengthened lead which comprises extruding a powder consisting essentially of lead having at least .7% lead oxide coating thereon calculated as PbO at an extrusion pressure chosen such that the process of extrusion breaks up the oxide coatings on the lead powder particles, distributes the resultant oxide fragments uniformly throughout the lead and causes the lead particles to become welded together, thereby producing a dispersion strengthened lead product without subsequent rolling.

12. The process of claim 11 wherein the lead particles are coated with from about 1 to about 16 weight percent of lead oxide, calculated as PbO.

References Cited by the Examiner

UNITED STATES PATENTS

2,113,279	4/1938	Olim et al.	
3,066,391	12/1962	Verdahl.	
3,098,293	7/1963	Ebdon	29—528
3,189,989	6/1965	Ebdon	29—420.5

JOHN F. CAMPBELL, *Primary Examiner.*

P. M. COHEN, *Assistant Examiner.*