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[54] **COPPER-LEAD ALLOYS FOR LUBRICANTS AND BEARINGS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 53,953, July 10, 1970, Pat. No. 3,719,477, which is a continuation-in-part of Ser. No. 706,640, Feb. 19, 1968, Pat. No. 3,556,779.

[52] **U.S. Cl.** ..... **252/26;** 252/56 R

[51] **Int. Cl.** **C10m 1/54;** C10m 3/48; C10m 5/28

[58] **Field of Search** ..... 252/26, 56 R

[56] **References Cited**

UNITED STATES PATENTS

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2,543,741	2/1951	Sweifel	252/26
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FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

This disclosure is directed to copper-lead alloys for lubricants and bearings. The copper-lead alloys have a fine and even dispersion of the lead particles in a copper matrix. The alloy is made by adding an effective amount of a homogeneity promoter to a mixture of molten lead and copper. The promoter comprises elemental carbon and an alkali and/or alkaline earth metal compound capable of reacting to form a gas, or a rare earth metal compound in the form of an oxide or carbonate.

The lubricants comprise the copper-lead alloy in powdered form, as a dry lubricant, in a carrier, or in a base of a grease or oil.

The bearings comprise the copper-lead alloy as a load-bearing surface.

16 Claims, No Drawings

COPPER-LEAD ALLOYS FOR LUBRICANTS AND BEARINGS

CROSS-REFERENCES

This application is a continuation-in-part of our copending application Ser. No. 53,953 filed July 10, 1970 now U.S. Pat. No. 3,719,477, which in turn is a continuation-in-part of our patent application Ser. No. 706,640 filed Feb. 19, 1968, now U.S. Pat. No. 3,556,779. This application is also directed to subject matter divided out of said applications.

DISCLOSURE OF THE INVENTION

This invention relates to lubricants and bearings of homogeneous copper-lead alloys. The term "homogeneous" is used herein to refer to an improved alloy having a fine and even dispersion of the phases.

Attempts to produce homogeneously dispersed copper-lead alloys have been made in order to provide such alloys which have high thermal conductivity, low electrical resistivity and a low coefficient of friction. These properties are highly desirable for metals used to make bearings or as a bearing material and as a dry lubricant or as an additive to liquid or viscous lubricants made of petroleum or vegetable bases. However, many problems have not been solved by the prior art in attempting to make homogeneously dispersed copper-lead alloys. The basic problem with these alloys is the prevention of massive separation and segregation of the copper and lead. This tendency to separate and segregate increases as the lead content rises in the copper-lead alloy. Another problem associated with the use of prior alloys is that even if there is initial homogeneity, under high stress and temperature conditions, the lead has a tendency to separate and segregate from the copper. A further problem associated with copper-lead alloys in the prior art is that the lead tends to segregate from the copper when it is being remelted and recast into other shapes and forms.

It is therefore an object of the present invention to provide bearings, bearing materials, dry lubricants, and petroleum and vegetable based lubricants comprising a homogeneous copper-lead alloy.

Other objects will be apparent from a reading of the specification and claims of this application.

Briefly, in accordance with the present invention, the foregoing and other objects are accomplished by the use of copper-lead alloys which are made by adding effective amounts of a homogeneity promoter to the molten metal. The promoter may comprise elemental carbon and an alkali or alkaline earth metal compound which reacts under the molten conditions present during the alloying and casting of the copper and lead to form a gas. Details regarding the preparation of the alloy appear in our above-noted U.S. Pat. No. 3,556,779 and U.S. Pat. application Ser. No. 53,953. The mechanism provided by the promoter is one of inoculation of a fine dispersion of the lead particles in a copper matrix. Examples of such compounds are sodium carbonate and calcium carbonate. Promoters containing rare earth metals may also be used in this invention. Details regarding this promoter to make copper-lead alloys are set forth in copending Pat. application Ser. No. 62,338 filed Aug. 10, 1970 now U.S. Pat. No. 3,720,507.

Many procedures are available in the art for making and using alloys, for example, see U.S. Pat. No. 3,544,314. However, the use of the homogeneity promoters described in the present and related applications leads to copper-lead alloys having a finer and more uniform dispersion of lead in copper and such alloys are particularly suited for use in bearings and lubricants.

Copper-lead alloys for use in the present invention are produced in varying proportions of copper and lead. The proportions may be varied as desired and as the specific application dictates. It has been found that alloys of substantial utility are those which contain 5 to 55% lead and 95 to 45% copper. The problem of separation and segregation of the lead and copper is greatest with a high lead content. The promoter of this invention therefore provides its greatest utility at lead contents of from 20 to 45%. If the lubricating qualities of the alloy are to be increased, the proportion of lead should be in the higher range. If it is desirable to increase the strength of the material, a lesser proportion of lead should be utilized. Additional elements may be added for their well-known enhancement of particular properties such as zinc, tin, nickel, etc., in amounts up to about 10% by weight of the alloy. The copper-lead alloy used in this invention may contain significant amounts of aluminum to harden the alloy, for example, up to about 10%. The details regarding the preparation of such alloys are set forth in patent application Ser. No. 112,421 filed Feb. 3, 1971.

As to the homogeneity promoter used for alloys in this invention, it has been found that the elemental carbon component is preferably finely powdered graphite. Although coarser carbon may be used, the larger particles tend to decrease the efficiency of the process, presumably due to reduced surface area to volume ratio. Other forms of carbon include bone-black, carbon-black, charcoal and the like.

The alkali metal compound may be lithium, potassium or sodium (or other metals of Group 1*a* of the Periodic Table), preferably combined as a carbonate. The alkaline earth compound may be calcium, strontium or barium (or other metals of Group 2*a* of the Periodic Table), preferably combined as a carbonate. Combinations of alkali and alkaline earth compounds may be used, for example, a mixture of sodium and calcium carbonate. The terms "rare earths" and "rare earth carbonates" as used throughout this application are intended to include scandium, yttrium, lanthanum and the lanthanides, the latter term encompassing those metals having atomic numbers from 58 to 71. The preferred rare earths are cerium and yttrium and mixtures thereof with lanthanum, praseodymium, samarium and europium. The preferred rare earth compounds are the halocarbonates, particularly the fluorocarbonates of the above metals. The carbonates and oxides of the rare earths are also suitable. The rare earth compounds may be used with or in place of the alkali and/or alkaline earth compounds.

The amount of homogeneity promoter used must be at least that amount which ensures formation of a uniformly dispersed mixture of lead and copper which does not segregate on solidification. A preferred effective range of the proportions has been found to be about 1–5 grams of carbon or graphite powder and about 3–15 grams of metal compound for each pound of alloy. Below this proportion improvements in homo-

geneity are obtained, but the effect is less pronounced when a very minor amount of promoter is used. Higher amounts of the homogeneity promoter may be used, for example, up to 10 grams of graphite and 30 grams of the metal compound for each pound of alloy. Although these and even greater amounts provide an improved alloy in accordance with the present invention, the use of greater amounts from an economic standpoint is less attractive. The maximum proportion of the promoter is determined by characteristic requirements of the alloy and economic considerations.

Although the exact mechanism is not completely understood, and patentability is not dependent thereupon, it is believed that the promoter is partially decomposed to form gases which provide a stirring and nucleation effect and that the undecomposed portion of the promoter also provides nucleation sites. The carbonate melts well below the reaction temperature range and decomposes at the higher temperatures into carbon monoxide gas and the metal oxide. The oxide in turn is reduced by the carbon to form additional carbon monoxide and metal. The metal may also be above its boiling point and released in gaseous form. The combined action of the gases cause the vigorous stirring action. Agitation continues through the cooling step and it is in this stage when the agitation is believed to be most effective. The agitation prevents gross separation of the lead and the copper phases and further provides many more nucleation sites for the solid, copper-rich dendrites to form from the liquid. The additional nucleation sites cause the final solidified structure to be fine-grained and further allows more efficient and homogeneous entrapment and entrainment of the lead phase in the copper matrix. Also, innoculation occurs by unreacted (or partially reacted) carbonate and graphite during stirring of the melt. The innoculation by these particles which are not fully decomposed to gases provides sites for the nucleation and growth of fine lead particles. The combined action promotes a random, fine-grained dispersion of lead in copper which is mandatory for the optimum characteristics and requirements of a bearing alloy and lubricant. An additional benefit of the emission of carbon monoxide, or gaseous metal, is to produce a reducing atmosphere over the alloy during the liquification and solidification which almost completely prevents oxidation of the alloy from the air. Thus, it is not necessary to employ artificial protective atmospheres to reduce severe metal loss due to oxidation. However, if desired inert atmospheres may be used in addition to blanket the system.

The novel copper-lead alloys used in this invention have a finer and more uniform dispersion of the lead in the copper. The composition of the alloy is from 5 to 55% lead, preferably 20 to 45% lead, 95 to 45% copper, preferably 80 to 55% copper, with up to 10% of other metals, preferably zinc and/or tin, with only minor amounts of other metals, and trace amounts of the homogeneity promoter. This copper-lead alloy may also be used in an aluminum matrix, as set forth in the above-noted patent application Ser. No. 112,421.

The average particle size of the lead in the copper matrix is between 0.002 to 0.020 mm diameter. Larger particles of lead occur but only a very minor amount of segregation occurs, which is not detrimental. An average particle size of 0.002 to 0.010 mm for copper-lead alloys having 20 to 45% lead produces an excellent alloy for use in the present invention. The average particle size remains within the above ranges even after the alloy is remelted or recast, although some minor agglomeration does occur.

The term segregation as used in this application is intended to refer to lead particles having a diameter greater than about 1 mm. The alloys of this invention have only a minor amount of segregation, preferably about 0%. The massive segregation which occurs without the homogeneity promoter of this invention is normally exhibited as a layering of the lead. Minor segregation is evidenced by lead particles having a size of about 0.5 mm, but this is not a serious problem if such particles are well dispersed and constitute less than 5% of the lead volume.

Another advantage of this process is the remelt capability of the copper-lead alloy without substantial segregation. This effect is desirable particularly if the material is produced as a solid billet which is to be subsequently cast into a desired form. The remelt capability without undesirable segregation may be due to remnants of the homogeneity promoter remaining in the alloy, or may be a function of the fineness of the original dispersion.

Although the homogeneity promoter has a lingering effect in improving the homogeneity of the alloy it may be desirable upon successive remelts, or where the original alloy composition remains molten for an extended period of time, to add the homogeneity promoter in increments. For example, when the alloy remains molten for a period of 10 minutes to an hour, a second addition of the promoter in an amount within the preferred effective range should be made prior to using (i.e., casting) the alloy.

Additional additives may be used in combination with the above-described homogeneity promoter. For example, from 1 to 10 grams of a metal phosphate may be used, such as ortho lead phosphate, ortho cupric phosphate or ortho tin phosphate.

In one method of making the alloy used in the present invention, copper of the desired quantity is placed in a graphite crucible and brought to a temperature of 1,250°–1350°C using an induction heater. When the copper is melted and has attained the appropriate temperature, as for example about 1,275°C, the lead and the homogeneity promoter are added to the melt preferably with stirring. Thereupon violent agitation of the liquid mixture ensues with the formation of gas. The temperature of the mixture is maintained for at least 1 minute and preferably 3 minutes for best results. The melt is then allowed to cool through its solidification temperature during which time the agitation continues. After solidification the temperature of the alloy is permitted to drop to ambient levels preferably not too slowly. Surprisingly, in spite of the gas evolved during the solidification of the melt, the resulting solid structure of the ingot is free of porosity. After the mixture has been formed it may be cast at conventional temperatures such as 1,000°–1,100°C.

The novel alloys of copper-lead prepared by the foregoing method have the structural characteristics required to produce optimum antifrictional qualities. The purity is high since the alloy has been thoroughly deoxidized. Also, the homogeneity promoter is almost undetectable by emission spectroscopy analysis. The lead phase is finely and randomly dispersed throughout the copper matrix. These factors contribute to a low coeffi-

cient of friction in the lifetime of the bearing alloy. They also have a high thermal condictivity and low electrical resistivity. In addition, they may be sintered, fabricated and machined without losing their superior antifriction qualities.

The alloy made by the above procedure is particularly useful as a bearing surface. It is suited for use when high or low temperatures and high stresses are present. Most standard methods for making bearings and bearing surfaces may be employed. The bearing can be made by casting techniques, as set forth in greater detail in patent application Ser. No. 53,953. Additionally, powder metallurgical techniques are useful. As an example, in bonding the alloy of the present invention to steel, the alloy can be powdered utilizing an atomization method. The steel is heated until it turns blue (approximately 600°F) and the powder made from the alloy is then sprayed onto the steel surface. The heat from the surface of the steel bonds the copper-lead alloy to the steel on contact. Alternatively the powdered alloy can be preheated to soften or melt the surface of the powder which is sprayed upon a base surface. The base is preferably first grit-blasted to roughen its surface and the powder may be heated for spraying with an oxy-acetylene torch under slightly reducing conditions. This technique is suitable for adding a 1/16 inch layer to thrust bearing pads. The powdered alloy can also be sintered onto a steel backing to provide a thicker bearing surface. In another technique a very thin intermediate layer of, for example, tin or zinc, can be electroplated or flame sprayed onto the steel surface followed by the application of a coating of the copper-lead alloy, to provide an improved bond. The powdered alloy may also be added to a plastic backing, for example, with an adhesive, and cut to the desired shape of the bearing surface and then sintered onto the bearing surface. The bond is strong enough to resist high stresses that result from bearing forces while providing excellent bearing properties. The alloys may also be used in ordnance developments, such as for small arms ammunition, rotating bands for larger caliber shells or on the inside surface of gun barrels.

Another manner in which the alloy can be used is as an additive to lubricants. The alloy is combined in powdered form with other lubricants such as greases and oils in quantities ranging preferably from a trace to four ounces per pound of the grease or oil. The resulting combination is a lubricant which fully coats moving parts thereby increasing the life of these parts. Maintenance requirements are also reduced. The alloy is of value when the lubricant combination is used in sealed units where frequent changes of lubricant are uneconomical. In this application the improved results are obtained over a longer period of time when higher percentages of lead are used in the alloy.

In greases, powdered copper-lead alloys are preferably used in amounts from about 15 to 25%, although higher or lower amounts can be used. For example, substantial amounts of the additive can be used in greases for heavy duty gears. In oils, particularly conventional motor oils, lesser amounts are used, for example from about ¼ to 5% of the alloy based on the weight of the oil, and depending upon the tolerances and wear of the bearing surfaces. The repeated addition of minor amounts is a suitable technique, such as 2 ounces every 10–15 thousand miles in the crankcase of an automobile.

The alloy may also be used as a dry lubricant, or in a minor amount of a carrier such as an oil or grease or a volatile organic compound, which is sufficient to facilitate application of the alloy to a bearing surface. In this manner the alloy can be applied to such surfaces as aluminum sliding doors and windows, or sliding electrical contacts. Plastic, rubber or fiber surfaces can also be treated with the powdered alloy under conditions of heat or pressure, or during fabrication techniques such as molding. In this manner the additive can be used on snowmobile plastic support members which are in contact with the underside of the rotating drive belts.

This invention will be illustrated in greater detail by reference to the following embodiments.

EXAMPLES 1–6

In these examples the alloys contained copper to lead in weight proportion of 60 to 40; the total weight of each ingot was one-fourth of a pound. The copper was heated to about 1,275° in a crucible in an induction oven. At this temperature the balance of the lead was added to the copper together with the components shown in the table below. The proportion of components added are listed in grams for each pound of the total of copper and lead. Results are tabulated as percent segregation in the alloy metals.

Table

Example	Na_2CO_3	Graphite Powder	Percent Segregation
1 (Control)	—	—	100
2	22.5	—	5–10
3	22.5	6.8	0
4	4.5	4.5	0
5	—	12.5	25
6	2.3	4.5	20

Examples 3 and 4 resulted in alloys of suitable quality for bearing materials.

EXAMPLE 7

A powdered mixture was prepared from 2.2 pounds of graphite and 4.8 pounds of sodium carbonate. The mixture was added to a molten alloy comprising approximately 20% lead, 4% zinc, 75% copper and minor amounts of antimony, nickel and other constituents. The bath contained about 400 pounds of metal at about 2,300°–2,400°F. The molten metal was then centrifugally cast by conventional procedures to form a motor support bearing. The casting proceeded smoothly and the molten metal flowed very well under the centrifugal pressure. Upon cooling the bearing was broken in a press and the internal structure visually examined. It was observed that excellent dispersion of the constituents of the alloy was obtained.

EXAMPLE 8

Nine pounds of copper were placed in an induction heater and brought to 1,300°C. Six pounds of lead and a mixture of 68.1 grams of sodium carbonate and 34.1 grams powdered graphite were added to the molten copper. The melt was held at 1,294°C for 2 minutes while being stirred with a graphite rod. The melt was then poured into a split graphite mold, 3 inches in diameter. The casting was allowed to cool for 1 hour and then removed. The casting showed no lead sweat on its outside surface. It was split and a physical examination

showed no lead segregation. A photomicrographic examination of the structure showed a fine dispersion of the constituents. Photomicrographs of the product appear as FIGS. 1 and 2 in Ser. No. 53,953.

A lineal analysis was made of the particle size and spacing of the product. The specimens were measured on a microscope with a Filar eyepiece that was calibrated in millimeters. Random traverses were conducted in a linear fashion across the surface of the metallographically prepared surface. Three traverses were run with about 200 measurements per traverse. Then the specimen was prepared with a surface perpendicular to the original surface and two more traverses were conducted at 200 measurements per traverse.

The resulting data were treated statistically. Standard deviations were calculated and are presented below.

	Average Particle Size	Standard Deviation	Average Distance Between Particles	Standard Deviation
Traverses Perpendicular to Axis of Ingot				
Traverse No. 1	0.0043 mm	0.0020 mm	0.0086 mm	0.0096 mm
Traverse No. 2	0.0043 mm	0.0021 mm	0.0083 mm	0.0082 mm
Traverse No. 3	0.0043 mm	0.0030 mm	0.0086 mm	0.0080 mm
Traverses Parallel to Axis of Ingot				
Traverse No. 1	0.0039 mm	0.0018 mm	0.0069 mm	0.0047 mm
Traverse No. 2	0.0037 mm	0.0015 mm	0.0069 mm	0.0045 mm

EXAMPLE 9

The same procedure set forth in Example 8 was repeated except that the promoter comprised 136 grams of lithium carbonate and 34 grams of powdered graphite. The melt was poured into the graphite mold which was surrounded with sand, which provided for a slower cooling of the casting. The casting provided an acceptable bearing material however it showed a minor amount of segregation.

EXAMPLES 10–12

Three castings were made, each weighing 15 pounds. The additive used was 136 grams sodium carbonate and 34 grams graphite in each example. The ratios of copper to lead were 60:40, 70:30 and 80:20, respectively. Each finished casting was then separately melted and poured into a high velocity stream of nitrogen to obtain a fine powder. The powders were sintered and compacted into bearing rings according to conventional techniques. The bearings were examined by the photomicrographic technique and showed a fine dispersion of the constituents. This evidences the excellent remelt capability of the alloys of the present invention and the capability of forming powders for a wide variety of industrial uses. The powder need not be made from a melt of the casting but may be formed directly from a mix of the molten metal and promoter.

EXAMPLE 13

A powdered mixture of a homogeneity promoter was prepared from one part of finely powdered graphite and four parts of sodium carbonate, by weight. The homogeneity promoter was added to a molten mixture of 60% copper and 40% lead at about 2,300°–2,400°F. The amount of the homogeneity promoter was 1 percent by weight of the molten metal. After 1 minute the molten mass was atomized in an inert atmosphere (nitrogen and argon are suitable) to form a powder. The powder which passed through a 325 mesh screen was collected; this powder had an average particle size of about 6 to 10 microns and was used in the following example.

EXAMPLE 14

The powdered alloy of Example 13 was used as a lubricant in automobile engines in amounts of from one-third to two-thirds of an ounce per quart of motor oil. Two ounces of the powder were mixed with one-half quart of 30W "Valvoline" motor oil and added to the crankcase of a Volkswagen (which already contained about 2½ quarts of oil) with the engine running. Prior to the use of the copper-lead additive, the car had been driven 62,000 miles and the average compression on the four cylinders was 100 pounds. After driving the car with the additive for 65 miles the engine compression was determined and found to have increased about 5% (compression 105 pounds), and after 700 miles the compression increased an additional 10% (compression 115 pounds). The examination of parts in contact with the copper-lead-oil lubricant showed that the alloy was burnished onto the bearing surface (a copper color in areas of wear was very noticeable).

This invention has been described in terms of specific embodiments set forth in detail. Alternative embodiments will be apparent to those skilled in the art in view of this disclosure, and accordingly such modifications are to be contemplated within the spirit of the invention as disclosed and claimed herein.

We claim:

1. A lubricating material comprising an oil or grease which has distributed therein a powdered homogeneous alloy, said alloy containing copper and lead and trace remnants of the products from a homogeneity promoter in molten copper and lead, said homogeneity promoter comprising elemental carbon and a metal compound selected from the group consisting of compounds of an alkali metal and an alkaline earth metal.

2. The lubricating material of claim 1 wherein said alloy comprises from a trace up to about 4 ounces of alloy per pound of oil or grease.

3. The lubricating material of claim 1 wherein said metal compound is sodium carbonate or potassium carbonate.

4. The lubricating material of claim 1 wherein said alloy comprises about 5 to 55% lead, and about 95 to 45% copper wherein the lead is in the form of a fine dispersion in a copper matrix, and the average diameter

of said lead particles is between about 0.002 mm to 0.02 mm.

5. The lubricating material of claim 1 wherein said alloy comprises about 20 to 45% lead, wherein the lead is in the form of a fine dispersion in a copper matrix, and the average diameter of said lead particles is between about 0.002 to 0.01 mm.

6. The lubricating material of claim 1 wherein said alloy has an average particle size of about 6 to 10 microns.

7. The lubricating material of claim 1 wherein said alloy comprises about 20–45% lead.

8. A composition comprising a powdered homogeneous alloy consisting essentially of copper and lead, and a homogeneity promoter which is the reaction product of elemental carbon with an alkali metal compound selected from the group consisting of sodium carbonate and potassium carbonate in molten copper and lead, and a petroleum or vegetable based lubricant.

9. The composition of claim 8 wherein the alloy comprises from a trace to 4 ounces per pound of said lubricant.

10. The composition of claim 8 wherein said alloy comprises about 20–45% lead.

11. A composition comprising a powdered homogeneous alloy comprising a mixture of copper and lead, wherein said mixture comprises from 5–55% lead and from 95–45% copper, and wherein the total of said lead and copper in said mixture is at least 90%, and trace remnants of the products from a homogeneity promoter in molten copper and lead, said homogeneity promoter comprising elemental carbon and a rare earth metal compound selected from the group consisting of oxides, carbonates and halocarbonates, and a petroleum or vegetable based lubricant.

12. The composition of claim 11 wherein the alloy comprises from a trace to 4 ounces per pound of said lubricant.

13. The composition of claim 11 wherein said alloy comprises about 20 – 45% lead.

14. A composition comprising a powdered homogeneous alloy comprising copper and lead, and trace remnants from a homogeneity promoter comprising elemental carbon and an alkali or alkaline earth metal compound capable of reacting to form a gas in molten copper and lead, and a petroleum or vegetable based lubricant.

15. The composition of claim 14 wherein the alloy comprises from a trace to 4 ounces per pound of said lubricant.

16. The composition of claim 14 wherein said alloy comprises about 20 – 45% lead.

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