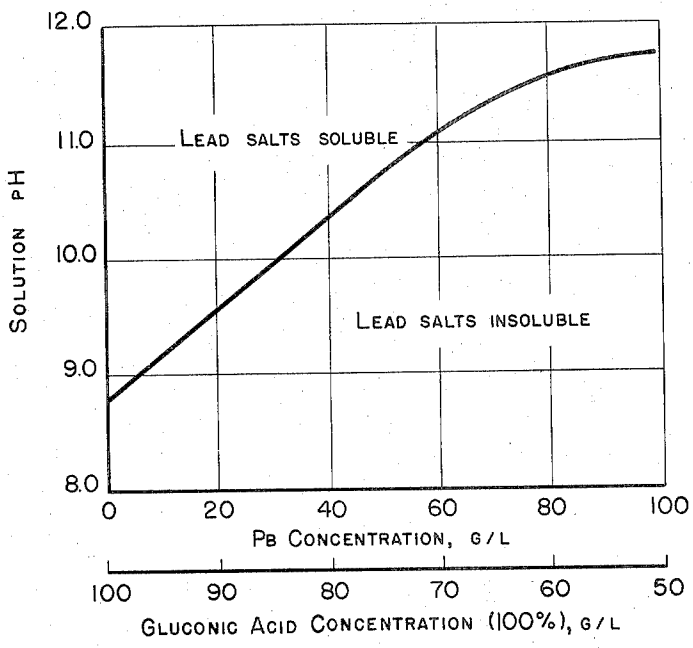
Sept. 18, 1956 W. G. HESPENHEIDE ET AL 2,763,606

ELECTRODEPOSITING BATHS AND PLATING METHODS

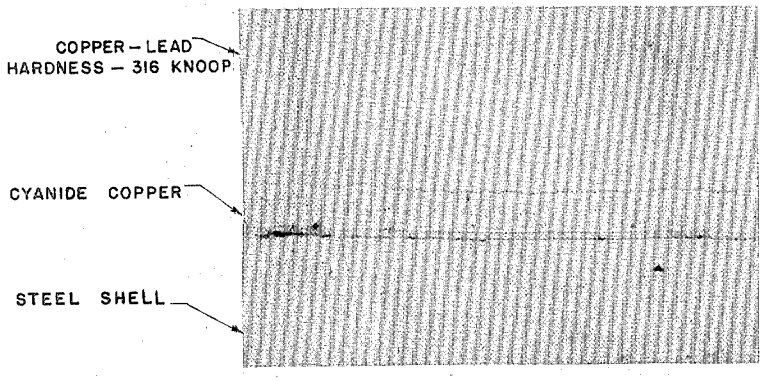
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FIG. 1



SOLUBILITY CHARACTERISTICS

FIG. 2

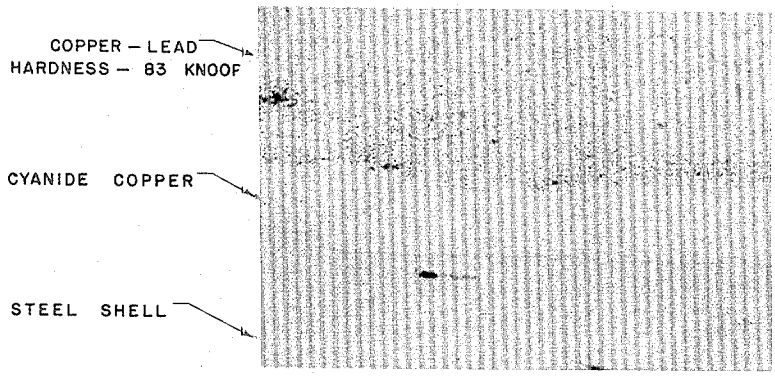


AS – DEPOSITED ALLOY LINING

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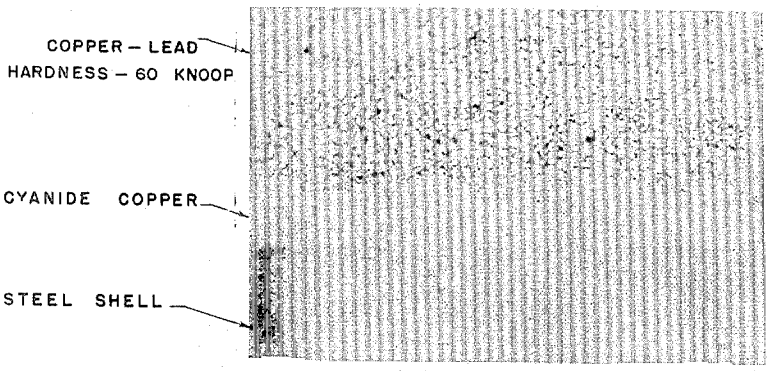
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ATTORNEYS:

FIG. 3



SAME LINING AFTER SALT IMMERSION
FOLLOWED BY WATER QUENCH
60 SECONDS AT 1250° F.

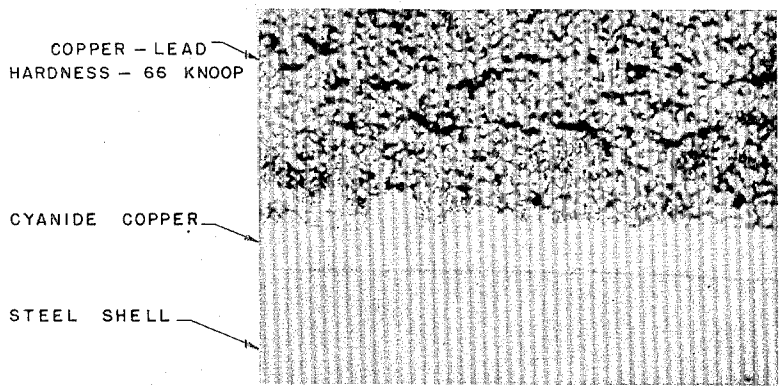
FIG. 4



SAME LINING AFTER SALT IMMERSION
FOLLOWED BY WATER QUENCH
120 SECONDS AT 1250° F.

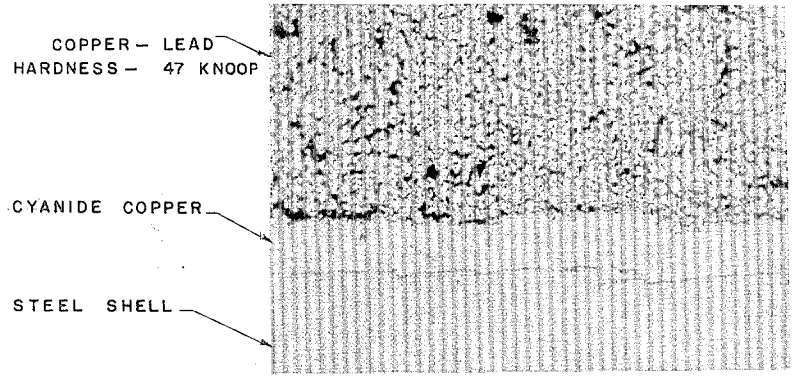
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FIG. 5



SAME LINING AFTER INDUCTION HEATING
FOLLOWED BY WATER QUENCH
15 SECONDS AT 1180° F

FIG. 6



SAME LINING AFTER ANNEALING
IN HYDROGEN ATMOSPHERE
19 HOURS AT 550° F.

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2,763,606

ELECTRODEPOSITING BATHS AND PLATING METHODS

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Application June 25, 1952, Serial No. 295,542

11 Claims. (Cl. 204—44)

This invention relates to electrodepositing copper-lead alloys. In particular, it relates to a method and bath for electrodepositing liners of copper-lead alloys on bearing shells of steel or other metal.

It is well known in the metallurgical field that copper-lead bearing liners have superior properties for use in heavy-duty service for industrial engines and machinery. According to present practice, copper-lead alloys are prepared by melting copper and lead together and then casting the molten metal on to the inside surface of a cylinder of steel or other metal. The copper-lead alloy may also be cast onto a flat strip of the proper thickness which is subsequently cut to the desired lengths and formed into bearing half shells. Due to the fact that the lead and copper are substantially insoluble in each other in the solid and liquid states, the copper-lead alloy bearing liners formed by these casting methods consist of a lace-work or dendritic structure of copper, surrounded by metallic lead.

During solidification of a mechanical mixture of copper and lead, the copper crystallizes in a dendritic structure, and the lead then solidifies in the region between these dendrites. This separation might be advantageous, especially if uniform, since the lead phase has a lubricating property which is highly desirable to bearing performance. However, such segregation of the lead, in addition to being non-uniform both in dispersion and concentration unless cast by very special and expensive techniques, also causes a serious disadvantage in the respect that there is a pronounced tendency for the lead to separate in a continuous layer at the interface between the metal backing element and the copper-lead alloy bearing layer. This interfacial layer of lead causes a zone of mechanical weakness, and consequently the performance of the bearing is not as satisfactory as it would be if the lead zone were not present between the metal backing member and the copper-lead alloy bearing liner.

Of course, enhancement of bearing performance is directly related to the extent and uniformity with which lead is dispersed in the copper matrix. Thus, lubricating effects are greatly increased, noise is eliminated to a greater extent, and the bearing is easier to machine. Prior attempts to prepare suitable copper-lead bearings by casting methods in which there is a satisfactory quantity, dispersion, concentration, and distribution of lead in copper have been retarded and made difficult by, among other factors, differences in the melting point of copper and lead; separation of lead upon cooling rather than an alloying thereof with copper; and the difference in specific gravity between the two metals.

For many years the bearing industry has sought ways to produce a copper-lead alloy bearing liner without the inherent disadvantages that result from preparing the alloy by melting and casting techniques. One of the methods proposed in the art is that of electrodeposition. Numerous suggestions have been made for electrodepositing copper-lead alloys, but none of them has produced an alloy plate which has the proper composition, say a composition in which copper predominates, and which at the same time, possesses the physical properties required for a bearing liner, as for instance a proper relation between copper and lead in the finished product.

The prior art copper-lead alloy plating developments have produced copper-lead electrodeposits that were either extremely brittle or wholly unsuitable for bearing liners due to the fact, for instance, that the codeposited copper and lead were noncoherent and appeared as a powdery-sponge-like metal. Further, the codeposits of copper and lead reported in the technical literature are extremely hard, not being amenable to customary metallurgical heat treatments, and have, therefore, resisted annealing to the lesser hardness which is desirable for bearing metal.

It has been proposed, as a specific example, to codeposit copper and lead from a bath containing copper hydroxide and lead acetate. This deposit, however, is characterized by many hair line cracks forming an irregular network extending from the surface of the deposit to the face of the backing metal. Further, the deposit is laminar in form, layers of lead occurring between adjacent copper layers and also there is an irregular dispersion of lead in the copper matrix. As a consequence, the deposit is brittle and incapable of practical use, and in an attempt to properly and satisfactorily relate the copper and lead phases, a special annealing technique is employed. However, a satisfactory softness can be attained only by annealing at temperatures above the melting point of lead for a prolonged period. This heat treatment causes the lead to sweat out forming an interfacial layer of lead as in casting techniques and also large aggregations of lead on the surface of the deposit. In addition, gross copper recrystallization grains are produced, and it will be seen that while the desired softness is attained, a much weakened structure is produced. This prior method for producing copper-lead bearing linings by co-deposition on a suitable backing is typical of what has heretofore been accomplished in the art.

It is well known in the art of alloy plating that there is no obvious equivalency between the methods for electrodepositing one or more pure metals directly and methods for electrodepositing alloys of these metals. In other words, the nature of the art is such that no suggestion or prevision is available which makes it possible to take a satisfactory electrodeposition bath for copper on one hand and for lead on the other, mix them together, and thus obtain a suitable copper-lead alloy plating solution which will thereby give an alloy having predetermined properties selected for a given usage.

There are, of course, known methods of alloy plating by which alloys of two or more metals can be formed. These are especially useful when other methods, such as melting and casting, are unsuccessful. Again, however, that same knowledge does not teach the procedure by which known plating methods can be combined, to immediately produce the desired results. All this is clearly shown by the known methods of electrodepositing copper and lead as pure metals. For example, copper can be deposited in good form for many uses from a copper fluoborate solution. Yet, when copper fluoborate and lead fluoborate are in the same solution, either a powdery, spongy, codeposit of copper and lead, or a very hard, extremely brittle codeposit of copper and lead is obtained, when alloys over 25 per cent copper are sought. Neither of these codeposits has been formed suitable for a bearing metal.

Likewise, it is known that copper can be deposited from a cyanide solution which contains free alkali as well as free cyanide. Lead has been deposited from a solu-

tion of lead oxide in an alkaline tartrate solution. Yet when the alkaline cyanide-copper solution and the alkaline tartrate-lead solution are mixed, the resulting solution will not produce a codeposition of copper and lead which is satisfactory for use in bearings.

A desirable and usable copper-lead alloy deposit might be expected if the teachings of alloy plating were directly transferable from one pair of metals to another. The technical literature shows that an alkaline silver cyanide-lead tartrate solution can electrodeposit a very satisfactory bearing alloy of high-silver and low-lead composition. Yet attempts to electro-deposit a suitable high-copper low-lead alloy from a comparable solution is totally without success.

It is recognized that codeposits of copper and lead can be obtained in a dense metallic form. However, this type of alloy is too brittle and too hard to be used as a bearing material, not being amenable to customary heat treatments for producing a product having suitable ductility and hardness.

In accordance with the present invention, it has now been found that suitable copper-lead alloys can be electrodeposited, particularly alloys in which copper predominates, and it has also been discovered that by means of a special heat-treating procedure, such alloys can be softened and rendered suitably ductile for use as a bearing material on a steel or equivalent backing member. Further, by the same technique to be described hereinafter, the copper-lead alloy plate can be electrodeposited on other bearing backing materials to produce a bearing-alloy liner.

The present process is based on a combination of copper and lead salts which has not heretofore been known or shown to be useful in electrodepositing alloys. For example, we have found that a combination of copper-cyanide and lead-gluconate produces a stable solution in water, and this solution is essentially capable of producing copper-lead alloy codeposits which can be subsequently heat treated to result in suitable bearing liners.

It is, therefore, an object of this invention to electrodeposit copper-lead alloys by a novel process.

It is another object of this invention to effectively electrodeposit copper-lead alloys on a metal backing material and to subsequently treat the alloys to produce a satisfactory bearing liner.

It is a further object of this invention to avoid in copper-alloy electrodeposits having a metastable solid solution of lead in copper, harmful segregations of lead that render such deposits detrimental for use as a satisfactory bearing material.

Yet another object of this invention is to produce satisfactory high-copper low-lead alloy electroplates.

Further objects should be apparent from what has hereinbefore been discussed and outlined, and other objects are also embodied in the description to follow as will be appreciated by those who are skilled in the art.

The desired alloy composition for most bearing use is in the range of 5 to 20% lead, balance copper, and it has been found that in accordance with the present invention, copper-lead alloys containing from 5 to 95% lead can be electrodeposited from cyanide-gluconate baths, and these baths are stable during long periods of continuous use, producing satisfactory deposits of copper and lead. Moreover, the desired high-copper, low-lead alloys are obtained in a form which can be suitably heat-treated by special techniques hereinafter to be described.

The alloy electroplates in this composition range are, according to X-ray examination, solid solutions of lead in copper since X-ray analysis in the present instance shows only a copper phase with a strained lattice. This solid solution is totally unpredicted by the usual thermal diagrams of copper-lead alloys, since the solubility of lead in copper certainly lies well below ½%, yet it is the result of the infinitely fine process of atom-by-atom electro-codeposition of copper and lead. The resulting solid

solution is very stable during low-temperature heat treatment. In view of the fact that this absolute condition of solubility of lead in copper, is thermally speaking, not a normal one, such solution occurring as the result of the present practice will be termed "metastable."

The plating bath for the copper-lead alloy electrodeposition comprises a water solution of gluconic acid to which has been added an alkali metal hydroxide, an alkali metal cyanide, copper cyanide, and a lead compound. In preparing the bath, the gluconic acid is first dissolved in water and the alkali metal hydroxide is added to adjust the pH to some value, preferably above 10, which will prevent the formation of hydrogen cyanide when the cyanide salts are added to the bath. An alkali metal cyanide, copper cyanide, and soluble lead compound are then added to the solution. A further adjustment in the pH, by addition of alkali metal hydroxide, may be necessary to permit a solution of the desired concentration of lead salts. Additional water can be added to adjust the volume, if necessary.

It appears that the alkali metal hydroxide and the gluconic acid form a soluble complex gluconate salt of the alkali metal and lead. The alkali metal cyanide and copper cyanide form a soluble complex, copper cyanide salt. Since lead forms no cyanide complex, it is necessary to have the lead so combined that there are as substantially few free lead ions in solution as there are copper ions in the solution of copper cyanide. Because copper forms no gluconic complex when cyanide is present, an excellent alloy electrodepositing bath is formed when lead gluconate complex and complex cyanide of copper and an alkali metal are present in the same solution.

In view of the fact that the lead apparently forms a complex salt with gluconic acid, the amount of gluconic acid suitable for use in the bath depends upon the composition of alloy desired, the pH of the solution, and other factors. However, satisfactory alloy coatings have been deposited using concentrations of from 2.5 to 50 cc./l. of gluconic acid. It may be desirable to use from 5 to 100 cc./l. of a 50 per cent solution of gluconic acid in water, since this material is more readily available.

The amount of lead to be added to the solution is also dependent on the desired composition of the alloy, the pH of the solution, and the concentration of gluconic acid. The lead may be added in the form of any soluble lead compound, and examples of such compounds include lead nitrate and lead dioxide. Fig. 1 shows the relationship between the pH of the solution, lead concentration, and gluconic acid concentration as it affects the solubility of lead salts. Satisfactory coatings have been obtained by maintaining from 0.1 to 10 g./l. of lead in the bath, such concentrations being maintained by periodic addition of lead salts or by the use of soluble anodes as will hereinafter be described.

The concentration of the copper cyanide also depends on the composition desired in the alloy coating. Satisfactory coatings have been formed from baths containing from 50 to 120 g./l. In general, a ratio of about three parts by weight of the alkali metal cyanide to two parts by weight of the copper cyanide is desirable in order to provide free cyanide in addition to the copper-alkali metal cyanide complex. This proportion will result in a free cyanide range of about 1 to 50 g./l.

As has been heretofore pointed out, the solubility of the lead salts increases with the pH of the bath. In this connection, it may be pointed out that a minimum pH of about 8.5 is required to dissolve the lead salts, a pH of from 10 to 13.5 representing the preferred range for depositing a bearing alloy coating. The temperature of the solution during electrodeposition should range from about 110° to 190° F.

In the electrodeposition of the alloy for use in a bearing, the bearing shell to be coated is made the cathode, the anodes preferably being made from an alloy having

approximately the same composition as that desired in the bearing liners. It is also possible to use pure copper anodes, and in this latter case periodic additions of suitable salts are necessary to maintain the desired concentration of lead in the bath. As an alternative arrangement, there may be provided individual anodes of lead and copper using a dual anode circuit. The areas of these latter anodes and the current supplied to each of them should be adjusted to maintain the desired rate of dissolution of the metals and thus replenish the metals plated from the bath.

The anodes can be stationary, suitably disposed about the axis of a cylindrical assembly, and agitation can be provided by continuously rotating, in one direction, paddles suspended from a disc between the anode and surface of the bearing shell, which is immersed in the plating bath. Alternatively, the anodes can be suspended inside the bearing shell and arranged to rotate. In the latter arrangement, it may be desirable to cyclically reverse the direction of rotation of the anodes to provide a "mixing-agitation" of the solution at the surface of the bearing shell. As a result, fresh solution is supplied to the anode and cathode surfaces during deposition, facilitating control of the physical properties of the plate. Suitable agitation may also be provided by moving the cathode if desired.

Although it is not necessary to provide a diaphragm or anode bags, their use is to be preferred. Very satisfactory coatings have resulted from enclosing the anodes in bags. When used with rotating anodes, the bags may be suspended so as to rotate with the anodes. For simpler control of the process, it is preferred to use a diaphragm having cylindrical shape surrounding the anodes. When rotating paddles are used as agitators, they should be separated from the anodes by the diaphragm. The diaphragm serves to contain any particles which may drop from the anodes, and prevents attachment of the particles to the plated surface with a resulting surface roughness.

Continuous filtration is also desirable and may be accomplished by withdrawing solution from the anode compartment and returning it to the cathode compartment. A filter press can be inserted in the line used for circulating the solution. This press may, or may not, use activated carbon for purification.

The current density will, of course, vary with the composition of the bath, temperature, agitation, etc. However, satisfactory coatings have been deposited with currents varying from 10 to 40 amp. per sq. ft. A periodic current reversal has been found to be beneficial in securing sound deposits, although its use is not essential in the present instance. The use of such a current tends to eliminate pitting and reduces the amount of roughness and columnar structure. However, there are instances wherein the reverse current may tend to cause brittleness and cracking of the plate.

It is preferable that the steel or other metal surfaces be given a copper strike plate by any of the conventional plating methods, such as is afforded by the use of a preliminary copper cyanide solution. The usual techniques of vapor degreasing, alkaline cleaning, dipping in hydrochloric acid, etc., are used to prepare the surface for the alloy coating. Where small dimensional tolerances are desired, the metal shells can be copper plated and then machined to the proper inside diameter. In such cases a thinner copper-lead alloy plate is desirable as compared to the alloy plate deposited over a copper strike plate. The bearing shell can then be made anodic in the copper-lead alloy plating bath, as a final cleaning operation, before being coated with the alloy.

The following examples will serve to illustrate the invention with greater particularity;

Example I

An alloy having a composition of 10 per cent lead and 90 per cent copper was deposited from the following aqueous bath:

Gluconic acid (50 per cent water solution)	cc./l. 50
Potassium cyanide	g./l. 180
Copper cyanide	g./l. 120
Lead dioxide	g./l. 2.4
Potassium hydroxide in sufficient amount to give a pH of 11.5.	

The bath was maintained at 120° F. The anodes were formed from an alloy of 10 per cent lead and 90 per cent copper, and were suspended inside the bearing and revolved at a rate of 150 R. P. M. A current density of 20 amp./sq. ft. was used, periodically reversing the current on a schedule of 3.5 seconds plate and 1.5 seconds deplate.

Example II

The following aqueous bath was used to form an alloy plating of 20 per cent lead and 80 per cent copper:

Gluconic acid (50 per cent water solution)	cc./l. 50
Potassium cyanide	g./l. 180
Copper cyanide	g./l. 120
Lead (as nitrate)	g./l. 2.1
Potassium hydroxide to raise the pH to 13.5	

The bath was maintained at 120° F., using anodes having a composition of 20 per cent lead and 80 per cent copper. The current density was 20 amp./sq. ft. and the cathode was oscillated at 66 R. P. M., using a 1¼ inch stroke.

Example III

An alloy having a composition of 45 per cent lead and 55 per cent copper was deposited, using the same operating conditions and bath as in Example II, except that the concentration of lead was 4.1 g./l., and the composition of the anodes was 45 per cent lead and 55 per cent copper.

Example IV

The same bath was used as in Example II, except that the lead concentration was 8.3 g./l. The bath was maintained at 140° F., and anodes having a composition of 90 per cent lead and 10 per cent copper were used. The current density was 20 amp./sq. ft. and the cathode was oscillated at a rate of 66 R. P. M., with a 1¼ inch vertical stroke. The deposited alloy had a composition of 90 per cent lead and 10 per cent copper.

After the copper-lead alloy has been deposited, it is necessary that it be annealed in order to reduce the hardness to a value suitable for bearings. Annealing at temperatures less than 800° F., commonly used for low-melting alloys, does not result in sufficient ductility, and causes the formation of two phases from the metastable solid solution of lead and copper. Before the desired softening can be accomplished, lead is sweated out of the alloy and appears on the surface of the bearing and in the interface between the alloy and the backing material as globules of pure lead or lead containing a small amount of copper. This physical structure is highly undesirable and detrimental to the performance of the bearing as was noted hereinabove.

In accordance with the present disclosure, subjecting the bearing to temperatures above 1000° F. for short periods of time in a nonoxidizing atmosphere will soften and anneal the copper-lead alloy plate or lines to a hardness value that is suitable for bearing metals. Induction heating can be used to accomplish this result, but the annealing of large bearing shells having a thin liner requires large and expensive induction heating equipment.

By the present method, annealing is carried out by immersing the "as plated" copper-lead alloy bearing shell in a fused salt bath at a temperature in excess of 1100° F. for periods of from 15 seconds to 4 minutes. By this procedure, the heating is so rapid, and the softening

so quick, that there is no harmful segregation or sweating out of lead, either in the matrix of the copper-lead bearing alloy or at the interface between the bearing alloy and the metal backing shell. To the contrary, lead is present in the form of small particles uniformly dispersed throughout the copper matrix.

In general, any suitable salt bath may be used for annealing the as-deposited alloy. The following annealing bath, as an example, was found to be very satisfactory:

	Percent by weight
Sodium chloride	20
Potassium chloride	25
Barium chloride	53
Calcium chloride	1
Borax	2

The time of immersion varies with the temperature of the bath, thickness of the coating and size of the article. However, it has been found that immersion for a period of from 15 to 120 seconds will provide a satisfactory anneal. The article should be quenched in water, oil or some other suitable liquid shortly after removal from the salt bath. The total time between immersion and quenching should not exceed 5 minutes for the best results.

Fig. 1 shows the relationship between the pH of the solution, lead concentration, and gluconic acid concentration as it affects the solubility of lead salts.

Figs. 2, 3 and 4 show the microscopic structures as deposited on a steel backing, and after annealing in the fused salt bath.

Fig. 2 shows the as-deposited alloy which has a hardness of 316 Knoop, there being a flash coat of copper from a copper cyanide solution intermediate the deposited alloy and steel shell.

Fig. 3 shows the same alloy plate after immersion in molten salt of 1250° F. for 60 seconds, followed by water-quenching. The hardness was reduced to 83 Knoop.

Fig. 4 shows another sample of the same alloy plate after immersion for 120 seconds in a molten salt at 1250° F., followed by water-quenching. The hardness was further reduced to 60 Knoop.

Figs. 3 and 4 clearly reveal that the alloy structure was changed, but there was no segregation of lead at the interface between the alloy plate and the copper-coated steel, and no detrimental segregation or agglomeration of lead in the alloy or at the surface.

The copper-lead alloy can also be annealed by heating to a relatively low temperature in a hydrogen atmosphere. Figs. 5 and 6 illustrate the effect of such low-temperature annealing.

Fig. 5 shows a sample of the same alloy plate illustrated in Fig. 2 except that it was heated to a temperature of 1180° F. by induction for 15 seconds and then water-quenched.

Fig. 6 shows this same sample after annealing for 19 hours at a temperature of 550° F. in a hydrogen atmosphere. While there was some recrystallization of copper and redistribution of lead, there was no segregation of lead between the copper flash plate and the copper-lead alloy plate, and also no harmful agglomeration of lead in the alloy or at the surface.

Although the preceding description of the novel copper-lead alloy coating and the process for depositing it have been described for use in forming bearing liners, the alloy can be electrodeposited by other techniques and equipment commonly used in the plating industry. For example, a satisfactory copper-lead coating can be formed on a flat panel which is suspended from a moving work bar oscillating back and forth in the plating solution. The plate can also be deposited in a closed circuit in which the solution is circulated by pumps and flowing at a suitable rate in a tube or pipe. The tube or pipe is then coated with the alloy electroplate.

From the foregoing it will be seen that by the present invention copper-lead electro-codeposits may be obtained in satisfactory form, and particularly in the case of bearing linings such deposits may be suitably obtained in the form of high-copper low-lead alloys. There has also been disclosed a subsequent annealing process by which the hardness of the alloy plate may be reduced without segregation of the lead in the alloy and without formation of any lead interface layer between the alloy coating and the base materials. It will be appreciated that this annealing procedure is particularly advantageous from a time standpoint.

Thus, while we have illustrated and described the preferred embodiments of our invention, it is to be understood that these are capable of variation and modification, and we therefore do not wish to be limited to the precise details set forth, but desire to avail ourselves of such changes and alterations as fall within the purview of the following claims.

We claim:

1. A copper-lead alloy electrodepositing bath capable of producing a solid solution of lead in copper which is substantially uniform in cross-section and free of surface and body irregularities comprising, an aqueous solution of from 50 to 120 g./l. copper cyanide, sufficient lead gluconate to provide from 0.1 to 10 g./l. lead, from 1 to 50 g./l. free cyanide, and sufficient alkali metal hydroxide to provide a pH of at least 8.5.

2. A copper-lead alloy electrodepositing bath capable of producing a solid solution of lead in copper which is substantially uniform in cross-section and free of surface and body irregularities comprising, an aqueous solution of from 50 to 120 g./l. copper cyanide, sufficient lead gluconate to provide from 0.1 to 10 g./l. lead, from 1 to 50 g./l. free cyanide, and sufficient alkali metal hydroxide to maintain lead in solution.

3. A copper-lead alloy electrodepositing bath comprising an aqueous solution prepared of from 50 to 120 grams per litre copper cyanide and from 1 to 50 grams per litre free cyanide to deposit copper, from 0.1 to 10 grams per litre soluble lead compound and from 2.5 to 50 cc. per litre of gluconic acid to deposit lead simultaneously with copper, and sufficient alkali metal hydroxide to maintain lead in solution.

4. The method of electroplating an article serving as a cathode with a copper-lead alloy lining comprising passing an electric current through an aqueous electrodepositing solution prepared of from 50 to 120 grams per litre copper cyanide and from 1 to 50 grams per litre free cyanide to deposit copper, from 0.1 to 10 grams per litre of soluble lead compound and from 2.5 to 50 cc. per litre of gluconic acid to deposit lead simultaneously with copper, and sufficient alkali metal hydroxide to maintain lead in solution.

5. The method according to claim 4 including the additional step of heat-treating the plated article to obtain a copper-lead alloy lining of bearing softness.

6. The method of providing a bearing lining on a bearing shell comprising electrodepositing a copper-lead alloy bearing liner on said shell by passing an electric current from an anode to said shell, serving as a cathode, through a bath prepared of from 50 to 120 grams per litre copper cyanide and from 1 to 50 grams per litre free cyanide to deposit copper, from 0.1 to 10 grams per litre soluble lead compound and from 2.5 to 50 cc., per litre of gluconic acid to deposit lead simultaneously with copper, and sufficient alkali metal hydroxide to maintain lead in solution.

7. The method according to claim 6 including the additional steps of annealing the plated bearing shell at a relatively high temperature.

8. A copper-lead alloy electrodepositing bath for depositing lead copper simultaneously and containing essentially of an aqueous solution of soluble complex copper cyanide and free cyanide, alkali metal hydroxide, and complex lead gluconate.

9. A copper-lead alloy electrodepositing bath for de-

positing lead and copper simultaneously and consisting essentially of an aqueous solution of soluble complex copper cyanide and free cyanide, alkali metal hydroxide, and a soluble lead salt and gluconic acid forming complex lead gluconate.

10. The method of electroplating an article, serving as an electrode, with a copper-lead alloy comprising, passing an electric current through an aqueous electroplating bath consisting essentially of complex copper cyanide and free cyanide, alkali metal hydroxide, and complex lead gluconate.

11. The method of electroplating an article, serving as an electrode, with a copper-lead alloy comprising, passing an electric current through an aqueous electroplating bath consisting essentially of complex copper cyanide and free cyanide, alkali metal hydroxide, and a soluble lead salt and gluconic acid forming complex lead gluconate.

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