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DECOPPERING OF GUN TUBES

BY LEAD

by

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Abstract

A mechanism for the decoppering action of metallic lead on gun tubes is proposed in which it is assumed that lead melts, dissolves the deposited copper, and carries the copper out in the liquid. The proposed mechanism is shown to be reasonable based on the properties of lead and considering the lead-copper and lead-iron phase diagrams. Consideration of the impurities commonly present in lead indicates that iron, silver, and copper should not affect the decoppering action; antimony, arsenic, tin and zinc should decrease the effectiveness of lead; and bismuth should enhance the decoppering action of lead. Of other low melting metals, bismuth and bismuth-lead alloys should be more effective than lead, while all others should be less effective than lead in decoppering.

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INTRODUCTION

Most projectiles for large bore guns have rotating bands made of copper
or gilding metal, a copper-zinc alloy. On firing the projectile through the
tube, the rotating band is engraved by the rifling, contacting it throughout
the length of the tube. During this contact, some of the copper is deposited
on the rifling. These copper deposits can have a serious effect on the
interior ballistics of the projectile, affecting muzzle velocity, precision
and tube wear.

One method of reducing the amount of coppering of gun tubes is to add
metallic lead to the propelling charge. This lead is usually added as a foil
blanket around the forward end of the charge. The effect of lead foil addi-
tive in reducing coppering was discovered empirically and has been used with
considerable success, though with no real understanding of why it works.
A mechanism for the decoppering action of lead has been proposed[1] in which
it is assumed that the lead forms a brittle alloy with the deposited copper,
which is then carried out of the tube with the next round containing no
decoppering additive. This mechanism is very unlikely since lead does not
alloy with copper to any measureable extent unless the copper is also melted.
The purpose of the present note is to propose an alternative mechanism for
the decoppering action of metallic lead and to show that the proposed mechanism
gives a reasonable explanation of the observed action.

Decoppering Mechanism

The mechanism proposed for the decoppering action of lead is as follows: (1) the lead melts and is deposited on the gun bore as liquid metal; (2) the liquid lead dissolves the deposited copper; (3) the liquid lead is then carried out of the tube as liquid droplets with the copper in solution. The process is visualized as one in which the copper-covered gun tube surface is wiped with liquid lead, allowing the lead to dissolve the copper and carry it out of the tube. To demonstrate that this mechanism is reasonable, several factors will be considered including the properties of lead, the lead-copper phase diagram and the lead-iron phase diagram.

Pure lead melts at 327°C and has a low heat of melting of 5.9 cal/g. It has a very wide liquid range, with a boiling point of 1620°C. Thus, it is clear that lead is easily melted; any metallic lead present would be expected to melt under the conditions present in a gun tube and would remain molten during the time it travels the length of the tube. Because lead has a fairly high boiling point, it would remain as a liquid rather than vaporizing, particularly if it is present at the cool boundary layer along the gun tube surface.

The lead-copper phase diagram is very simple, Fig. 1.[2] Lead and copper are insoluble in each other in the solid state, with the solubility of lead in solid copper extremely small all the way to the copper melting point. No intermetallic compounds form between copper and lead. Copper has only a slight effect on the melting point of lead and has a very small solubility in liquid lead at the lead melting point. The solubility of copper in liquid lead increases with increasing temperature above the lead melting point, as given by curve AC, Fig. 1. At 955°C, a monotectic reaction occurs, with two liquids above that temperature and one liquid below. Above the monotectic temperature,

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the solubility of copper in the liquid increases very rapidly with increasing temperature.

Based on the phase diagram, it is clear that, if there is a layer of copper on a surface, applications of liquid lead to the surface will allow some of the copper to dissolve in the liquid. Removal of this liquid after dissolving copper will then remove some of the copper from the surface. By application of sufficient liquid lead, any desired amount of copper can be removed from the surface. The dissolution process is assumed to occur by diffusion and convection in the liquid. If an intermetallic compound layer formed at the solid-liquid interface, then further dissolution would be limited by the rate of diffusion of copper through this solid compound layer. This solid diffusion process would be much slower than liquid diffusion and would severely restrict the dissolution rate of copper into the liquid. In addition the formation of this compound layer would deplete the amount of liquid available for dissolving copper. Thus the absence of intermetallic compound formation between copper and lead is important in allowing rapid dissolution of copper in the lead.

It should be noted that, because lead is not soluble in solid copper at any temperature below the copper melting point, the application of liquid lead to the solid copper does not cause the metals to alloy. Any lead which remains on the copper surface will remain as a ductile lead layer and not as a brittle lead-copper alloy. The only way to form lead-copper alloys is to melt the copper in conjunction with the lead, which is unlikely to occur in the gun tube. Thus the decoppering mechanism quoted in the introduction is very unlikely to occur.

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It is important to note that the proposed mechanism postulates that the lead removes the copper as a liquid, rather than as a vapor phase. If vaporization occurred, the lead would evaporate preferentially, leaving the copper behind. There is no evidence to suggest that lead and copper tend to associate in the vapor phase, as would be required for a vaporization process to be effective.

The interaction of liquid lead with the gun steel surface must also be considered. Liquid lead does not spread readily over an iron or steel surface[3]. Therefore, the liquid lead can deposit on the copper layer, dissolve it, and then be carried away very readily by the powder gas. The lead-iron phase diagram[4] is similar to that of lead-copper except that the solubility of iron in the liquid is much lower than that of copper. Thus, the lead will dissolve copper very readily, but will dissolve very little iron.

We must now calculate how much copper can be removed by the amount of lead used in a typical artillery round. For purposes of calculation consider the 155mm M549 round as fired in the XM199 gun tube[5]. The XM203E1 propelling charge used with this round contains about 160 grams of lead foil (1.3% of the total charge weight of 11.8kg). As noted above, liquid lead at 900°C will form a solution containing 6.7 weight percent copper. Thus, the weight of copper dissolved in 160 grams of lead is:

$$W_{dis} = \frac{0.067 \times 160}{0.933} = 11.5 \text{ grams.}$$

The rotating band on the M549 round is 5cm long. The 48 rifling lands of the gun tube engrave grooves in the rotating band which are about 0.8cm wide by 0.1cm deep, removing a total metal volume of:

$$V_{rem} = 0.1 \times 0.8 \times 5 \times 48$$

$$= 19 \text{cm}^3$$

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from the rotating band. The total weight of copper removed from the rotating band is then (using the density of copper, 8.92g/cm^3):

W_{rem} = 19 x 8.92

= 170 grams.

A small fraction of this removed copper will be rubbed onto the rifling and will remain in the tube as a copper deposit. If 5 percent, or 8.5 grams, of this copper remains as a deposit, then the lead in the charge is more than adequate to remove it. If as much as 20 percent, or 34 grams, of this copper remains as a deposit, then the lead in the charge is probably not sufficient to remove all of it. The major portion of the copper will be removed as bulk pieces during the initial engraving process and only a small amount will rub onto the rifling bands. Thus, one could estimate that the amount of copper deposited would be nearer 5 percent than 20 percent of the total copper removed from the rotating band. Based on this estimate, it is concluded that the lead added to the charge is just about adequate to remove the deposited copper. If the amount of lead were reduced by a factor of 3, then it would almost certainly be insufficient to do the job; if the amount of lead were increased by a factor of 3, then it would certainly remove all deposited copper.

The conclusion reached from the above considerations is that the proposed mechanism of decoppering by lead is reasonable and that the amount of lead used in present charges is near the optimum amount to insure adequate copper removal.

Discussion

Accepting the conclusion of the previous section, that lead removes copper by dissolving it in the liquid, there are several points that should be discussed in order to obtain the best results in selecting decoppering

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additives. The items to be discussed are (1) the selection of the amount of lead needed to be effective, (2) the effects of impurities in the lead on its decoppering effectiveness, (3) alternative low melting point metals for use as decoppering additives, and (4) the use of lead (or other) compounds for decoppering.

1. In order to select the amount of lead to include in the charge for decoppering, one must first determine how much copper must be removed. If there is full engraving of the round in the gun bore, then it is possible to determine how much copper is engraved from the band by knowing the extent of interference between the band and the rifling. It can then be estimated that from 5 to 20 percent of this copper remains in the gun tube and must be removed by lead. The amount of lead required is approximately 15 times the amount of copper which remains in the tube. For the example of the M549 projectile used above, about 170 grams of copper were removed from the rotating band. With 5 percent remaining in the bore, then 0.05 x 170 x 15 = 128 grams of lead must be used. If 20 percent remains in the bore, then 0.2 x 170 x 15 = 510 grams of lead must be used. Thus, the minimum lead addition must be around 150 grams per round. If the rotating band were pre-engraved, then less copper would be stripped from the band but about the same amount would be deposited in the bore. Again, one could estimate the amount of copper deposited and use 15 times as much lead in the propelling charge.

The position of the lead foil in the propelling charge could affect the amount of copper that would be removed per unit mass of lead. Lead foil or shot homogeneously mixed with the propellant would probably not be as effective as foil placed around the forward periphery of the charge.

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2. Impurities in lead can affect its behavior as a decoppering agent. The common impurities are likely to be tin, antimony, arsenic, bismuth, iron, zinc, copper, and silver[6]. Iron and silver are just slightly soluble in lead and are very unlikely to affect the decoppering behavior. Copper would normally be present in an amount of 0.1 percent or less and this would not be deleterious. If, however, the lead had copper mixed in to the extent of several percent, then this copper would tend to saturate the liquid lead so it would not remove as much copper from the tube as expected.

Tin, antimony, arsenic, and zinc can go into solution in the copper or react with it to form intermetallic compounds. These processes do not remove copper from the tube, so that the portion of the lead taken up by the impurity is not effective. Thus, relatively more lead must be added to make up for the presence of the impurity. These elements can also react with the iron of the steel tube to form intermetallic compounds. The effect of this would be to form additional bore deposits, rather than remove the copper as desired.

Bismuth, as an impurity, would probably promote the decoppering action of lead, as discussed in the next section. Bismuth has a higher solubility for copper than does lead and has a lower melting point than lead; both of these properties would tend to make bismuth more effective than lead in removing copper.

In conclusion of this section, tin, antimony, arsenic, and zinc as impurities in lead would decrease its decoppering action. Bismuth would help the decoppering action, while iron, silver, and copper would not have much effect.

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3.   It is interesting to consider other low melting metals which might have decoppering action similar to that of lead. In Table I are the elements which are candidate materials, listed according to their column in the periodic table. These elements all have relatively low melting points, so they would probably melt under the conditions in a gun tube.

Consider first the alkali metals, lithium, sodium, potassium, rubidium, and cesium. Lithium has a low melting point and a high boiling point. Also, there are no Li-Cu or Li-Fe intermetallic compounds, and copper is appreciably soluble in liquid lithium. Therefore, lithium would have good properties as a decoppering agent if it could be used in a charge. All the alkali metals, however, including lithium, react very strongly with air, water-containing materials and many other materials, so they would not be stable as part of a propellant charge. Therefore, the alkali metals must be eliminated as possible decoppering agents.

Zinc, cadmium, and mercury have low melting points, but they also have low boiling points, so they would tend to evaporate rather than remain as liquids. Thus they would not remove copper. In addition, zinc and cadmium react with copper to form solid solutions and intermetallic compounds, tending to remain in the tube rather than removing copper. Zinc also forms compounds with iron which would cause it to stay in the tube. Cadmium and mercury are undesirable because they have a tendency to cause embrittlement of steel. Therefore, zinc, cadmium, and mercury would not be useful as decoppering agents.

Selenium and tellurim have relatively low boiling points. In addition, they form quite stable compounds with copper and iron. Thus, selenium and tellurium would not be good decoppering agents

TABLE I

Elements with Low Melting Points

Element	Melting Point ($^{\circ}$C)	Boiling Point ($^{\circ}$C)
Li	181	1330
Na	98	892
K	64	760
Rb	39	688
Cs	29	690
Zn	420	906
Cd	321	765
Hg	-39	357
Ga	30	2237
In	156	2000
Tl	303	1457
Sn	232	2270
Pb	327	1725
Bi	271	1560
Se	217	685
Te	450	990

Gallium, indium, and tin all have low melting points and high boiling
points. All three of these elements, however, form solid alloys and inter-
metallic compounds with copper, so they would not remove the copper in the
liquid unless a very large amount of the element were added to the charge.
The low melting point of gallium would make it difficult to add to a charge
since the metal would melt at temperatures only slightly above room tempera-
ture. In addition, gallium is a relatively rare material and would be very
expensive if it were possible to obtain enough to add to all charges. Indium
is also a relatively rare, expensive material. Thallium has properties simi-
lar to those of lead in its physical characteristics. It is, however, very
toxic and would be difficult to handle with an adequate degree of safety.
Based on these considerations, then, the metals gallium, indium, thallium,
and tin must be eliminated as decoppering agents.

The only metal that is left in addition to lead is bismuth. This metal
has melting and boiling points somewhat lower than those of lead. The copper-
bismuth phase diagram is shown in Fig. 2[7]. There are no intermetallic com-
pounds between copper and bismuth. There is extremely small solid solubility
of copper in bismuth and of bismuth in copper. Copper is more soluble in
liquid bismuth than in liquid lead, having a solubility of about 50 weight
percent copper in bismuth at 900°C. Bismuth wets copper much better than
does lead, having a tendency to penetrate copper grain boundaries; thus, cop-
per would probably dissolve more rapidly in bismuth than in lead. Bismuth
also does not interact strongly with steel. Based on these properties of
bismuth, it appears that bismuth should be a more effective decoppering mate-
rial than lead. The amount of bismuth required for effective action should
be less than the amount of lead currently being used.

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An alloy of 55 percent bismuth - 45 percent lead has a melting point of $124^{\circ}C$, which is considerably lower than that of either of the pure metals. Thus, an alloy of this composition or alloys for a considerable range around the 55Bi- 45Pb composition could be very effective decoppering agents.

In conclusion of this section, it appears that bismuth or bismuth-lead alloys would be good alternatives to lead for tube decoppering. All of the other available metals have shortcomings which eliminate them as candidate materials. The principal deterrent to the use of these metals is the fact that they form solid solution alloys or intermetallic compounds with copper or iron or both. Bismuth appears to be promising enough as an alternate material that it would be well worthwhile to prepare and fire rounds containing bismuth rather than lead.

4. Because metallic lead has some deleterious effects on steel, consideration can be given to the use of lead compounds or other compounds in the charge as decoppering agents. There are three possible mechanisms by which a compound could remove copper from the gun tube.

a. The compound could melt and dissolve the copper, as proposed in the mechanism for the action of lead in an earlier portion of this paper.

b. The compound could react with the copper deposit to form a copper compound which is easily removable from the tube.

c. A lead (or bismuth) compound could be reduced to metal by the propellant gases, and the metal could remove the copper by the mechanism proposed earlier in the paper.

With regard to mechanism (a) there are very few compounds which melt at low temperatures and at the same time will dissolve metallic copper. In particular, compounds such as PbO, PbO_2, or $PbCO_3$ will not melt at low enough temperatures to dissolve copper in a gun tube.

Mechanism (b) above would be unlikely to occur because copper is less active than steel. Any compound added to the charge to react with copper would react even more strongly with steel. Thus, at any spot where the copper was removed by the compound, the compound would then continue to attack the steel, causing damage to the gun tube rather than removing the copper.

Mechanism (c) could be limited by the kinetics of reaction of the propellant gas with the lead or bismuth compound. For this mechanism to work, it would be necessary for the compound to be very rapidly reduced by the gas and have the metal collect on the tube walls to dissolve the copper. The liquid metal would then carry the copper out of the tube. This mechanism would require a special combination of circumstances. The compound would be reduced most readily in the hotter portion of the flame, while the reduced metal is utilized on the cooler tube walls. This combination would not be easily achieved in a real propellant system. If the compound were placed toward the center of the charge, it would be readily reduced but could not find its way to the walls before the charge was carried out of the tube. If the compound were placed along the outside of the charge, it might not be reduced in sufficient time to deposit the lead on the walls. This mechanism might possibly work with compounds such as PbO or $PbCO_3$, but conditions would have to be selected very carefully to get the optimum results.

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It is interesting to note that the effect of tin dioxide on tube decoppering has been investigated previously[8]. The conclusion of this study was that tin dioxide did not assist in decoppering. Very little tin was found in any of the barrel residues examined, but large amounts of coppering were found in every case, regardless of tin dioxide content. This result is in agreement with our conclusion that tin would not be an effective additive for decoppering.

In conclusion of this section it appears that compounds added to the propellant charge are not likely to be effective in removing copper from the tube in the same manner that metallic lead is effective.

There are, of course, so many organic and inorganic compounds available that it is not possible to state arbitrarily that none will work. Based on the discussion in this section, however, one can state with considerable confidence that almost no compounds are likely to be effective by these three mechanisms. Thus, an effective compound would be likely to act by some other mechanism.

Conclusions

1. A mechanism has been proposed for the decoppering action of metallic lead in gun charges. The mechanism assumes the lead melts, dissolves the deposited copper, and carries the copper out in the liquid.

2. The proposed mechanism is shown to be reasonable based on the known properties of lead and considering the copper-lead and iron-lead phase diagrams. Based on this mechanism, the amount of lead currently used in propellant charges is shown to be just about adequate. A method for calculating the estimated amount of lead required is demonstrated.

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3. The impurities commonly present in lead were considered and it was indicated that (a) iron, silver, and copper will not affect the decoppering; (b) antimony, arsenic, tin, and zinc will decrease the decoppering effectiveness; (c) bismuth will increase the decoppering action.

4. A large number of low melting metals were considered as alternate materials to lead as decoppering agents. It was concluded that bismuth and bismuth-lead alloys might be even more effective in decoppering than is lead. All other low melting metals would probably not work as well as lead in decoppering.

5. It was indicated that additions of inorganic compounds to the charge for decoppering are unlikely to be effective.
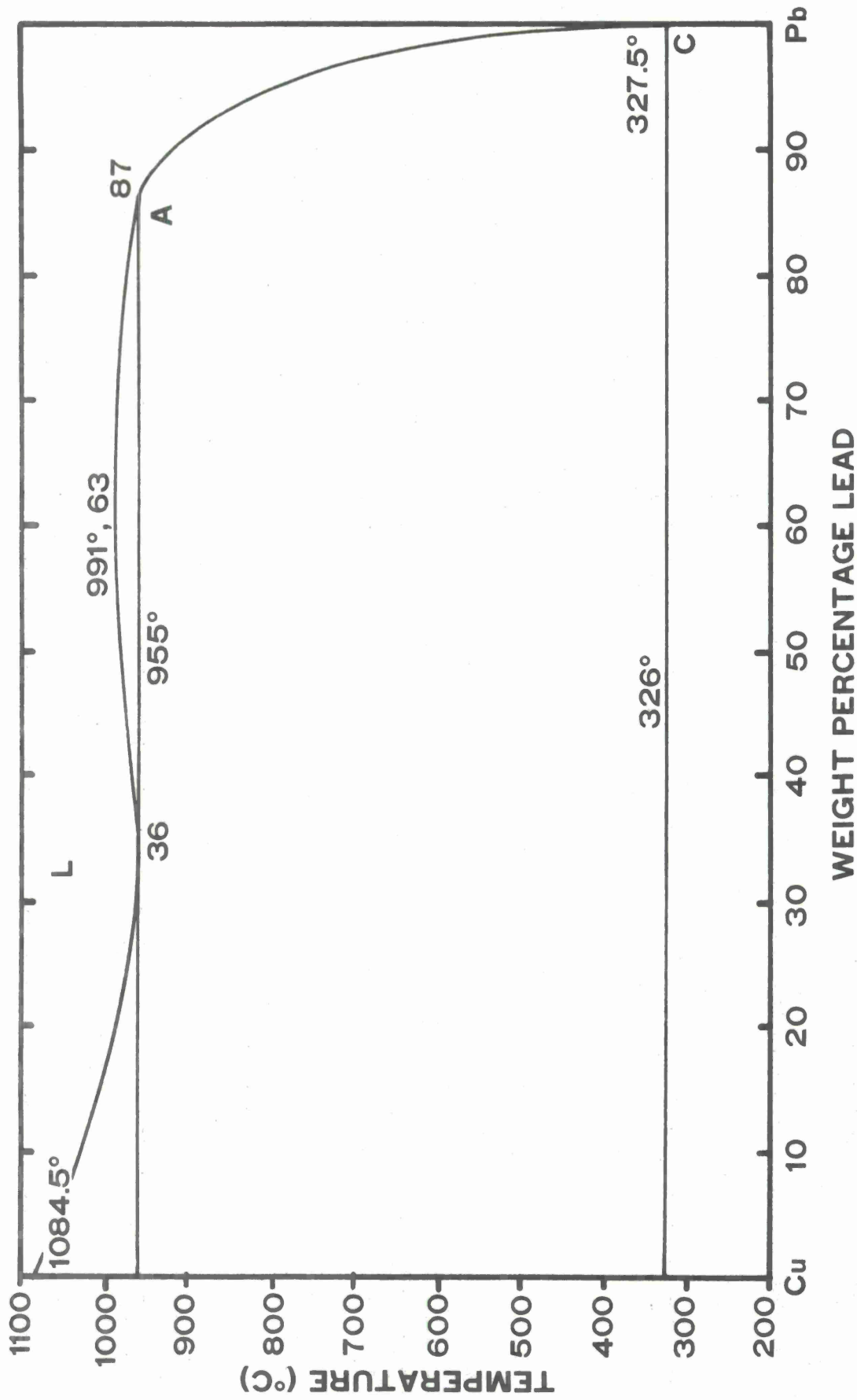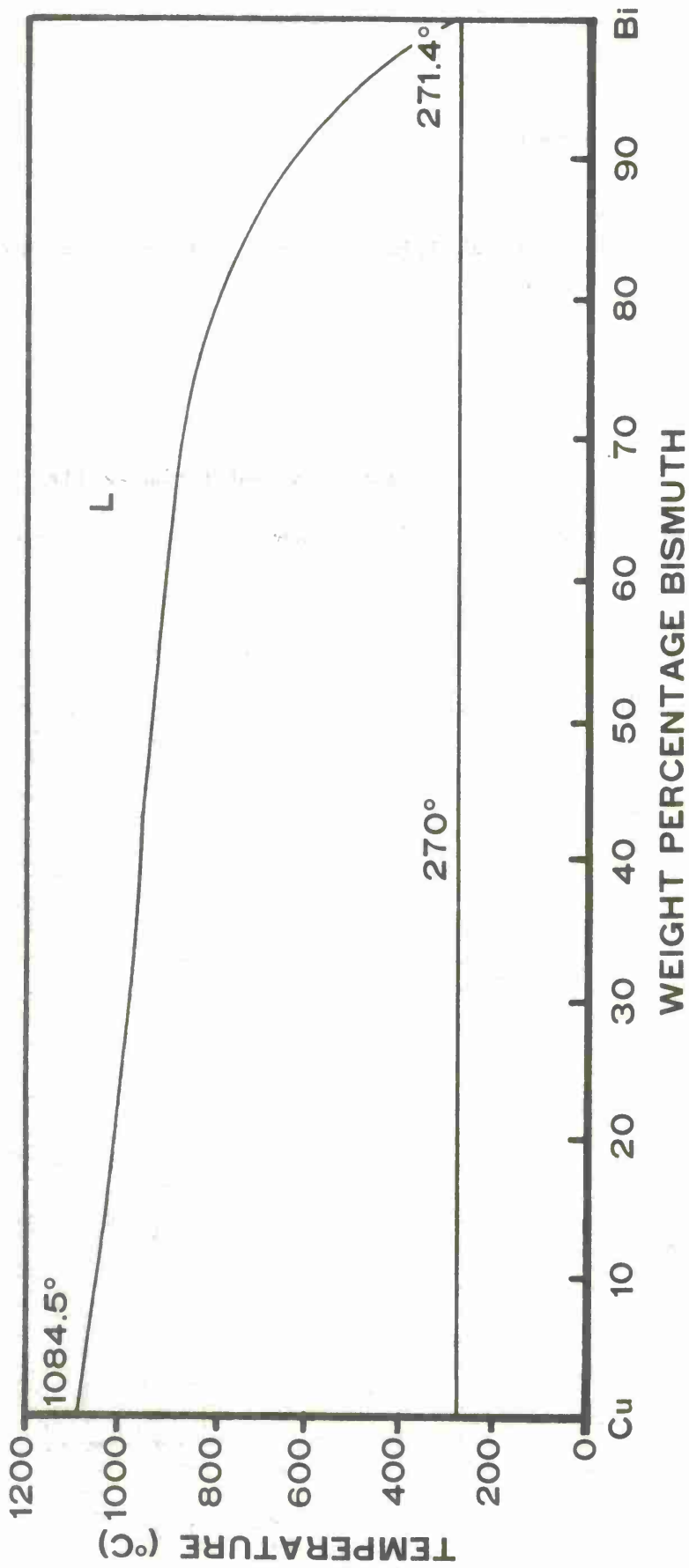
FIG. 1 COPPER - LEAD PHASE DIAGRAM

FIG. 2 COPPER - BISMUTH PHASE DIAGRAM

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