The present invention relates to precipitation hardenable copper base alloys and more particularly to a process for improving the properties of such alloys. In my copending application Serial No. 100,561, now Patent 2,225,339, December 17, 1940, and entitled "Precipitation hardened copper alloys," of which the present application is a continuation in part, there is disclosed a double aging process as applied to copper-chromium-beryllium alloys. I have found that the method disclosed in my prior application is applicable not only to copper-chromium-beryllium alloys but is in general applicable to all copper base precipitation hardenable alloys. However, for convenience and brevity my invention will be described particularly as applied to copper-chromium-beryllium alloys. Alloys of this composition are disclosed in the patent to Dahl, 1,847,929, and generally contain about 0.1% to 1% beryllium, about 0.4% to 6% chromium with the remainder copper.

The alloy disclosed in the Dahl patent is age or precipitation hardened by heating it to an elevated temperature, quenching and reheating to an intermediate temperature at which full or complete precipitation occurs, that is further precipitation cannot be effected by any further heat treatment alone. When precipitation hardened this alloy is relatively soft. I have found however that its properties may be improved by double aging, for example by superimposing a strain upon the completely precipitation hardened alloy and subsequently reheating or aging the strained alloy whereby a super normal precipitation may be obtained.

The expression "double ageing" as employed in the present specification and claims is the use of two precipitation reheat treatments with or without a previous solution treatment and with an intermediate straining treatment either thermal or mechanical. Any such alloy as that indicated above which is normally constituted of a single solid solution phase in the annealed (quenched) state may be double aged by the application of sufficient strain to the precipitation hardened alloy and by reheating for a sufficient length of time at temperatures below those effecting any recrystallization in the alloy.

I have found that double ageing may be effected in precipitation hardenable alloys by one of the following processes:

(a) Precipitation hardened, thermally strained then given a second aging treatment.
(b) Precipitation hardened, cold worked, then given a second aging treatment.
(c) No solution treatment, first aging, then applying a thermal strain and finally giving a second aging treatment.
(d) No solution treatment, first aging, cold working, then giving a second aging treatment.

Process (a) may be applied to certain aluminum base alloys, for example alloys of the following type:

5 Zn—1 Mg—2 Fe—92 Al
5 Si—0.5 Mg—1 Cu—93.5 Al
7 Si—0.3 Mg—92.7 Al

This process may also be applied to advantage to certain copper base alloys, for example:

5 Ni—5 Sn—0.2 to 2% Zn—88 Cu
7.5 Ni—8 Sn—0.2 to 2% Zn—92.5 Cu
20 Ni—7 Sn—0.2 to 2% Zn—71 Cu

Process (c) as set forth in my copending application Serial No. 247,488, filed December 23, 1939 may be applied to advantage to the following aluminum base alloys:

5 Si—1 Cu—0.5 Mg—93.5 Al
7 Si—0.3 Mg—92.7 Al

Process (d) may be applied to aluminum base alloys of which the following is an example:

0.7 Si—1.3 Mg—0.25 Cr—97.75 Al

The expression "thermal strain" as employed in the present specification and claims means a strain obtained by a controlled cooling from the first precipitation reheat, for example cooling at a rate to induce a condition of critical strain in the alloy, that is, water or oil quenching, or rapid air cooling.

The present invention is concerned principally with those alloys to which process (b) is particularly applicable. The copper base alloys, to which the present invention is directed, are mechanically strained by cold working, for example by producing a permanent change in dimension of the metal or alloy by mechanical means oper-
ating on the metal or alloy while they are at temperatures below that of recrystallization for the pure metal or alloy. Cold working to produce a uniform or regular change in dimension may be accomplished by swaging, forging, rolling, drawing or extruding. Cold working to produce localized change in dimensions may be accomplished by cold shaping or by a cold failure of the metal or alloy due to tension, compression, torsion or frictional wear.

In accordance with prior art precipitation hardening processes, if a cast rod about 1 1/4 inches thick and consisting for example of 0.4% chromium, 0.1% beryllium and about 99.5% copper is precipitation hardened by heating for about one hour at 900° C., quenching in cold water, cold swaging to about one inch diameter and then reheating at about 475° C. for an hour, the following properties are obtained:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>47,700</td>
</tr>
<tr>
<td>Proportional limit</td>
<td>30,000</td>
</tr>
<tr>
<td>Elongation</td>
<td>27</td>
</tr>
<tr>
<td>Hardness</td>
<td>Rockwell B. 63</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>per cent that of copper</td>
</tr>
</tbody>
</table>

The structure obtained in the cast rod by the above process is characterized by the presence of slip bands which are present in substantially all cold worked alloys. Also, the room temperature physical properties of the alloy are relatively unaffected by reheating up to about 400° C. and recolting.

If the 1 1/4 inch rods are heated for about one hour at a temperature of about 500° C., quenched in water, reheated at about 500° C. for one hour, air cooled and then mechanically strained by swaging to effect a reduction in diameter of about 50% the following properties are obtained:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>60,000</td>
</tr>
<tr>
<td>Proportional limit</td>
<td>40,000</td>
</tr>
<tr>
<td>Elongation</td>
<td>13</td>
</tr>
<tr>
<td>Hardness</td>
<td>Rockwell B. 72</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>per cent that of copper</td>
</tr>
</tbody>
</table>

The production of a mechanical strain in the alloy by cold working after precipitation hardening effects a marked increase in tensile strength, proportional limit and hardness and the resulting product is characterized by the comparative freedom from slip bands ordinarily present in cold worked material. The production of a mechanical strain in the alloy may of course be produced by any of the means hereinbefore set forth. If the precipitation hardened rod is now maintained or reheated at a temperature of about 100° C. for about 1 1/2 hours and air cooled the following properties are obtained in the double aged alloy:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>65,000-70,000</td>
</tr>
<tr>
<td>Proportional limit</td>
<td>43,000</td>
</tr>
<tr>
<td>Elongation</td>
<td>9-12</td>
</tr>
<tr>
<td>Hardness</td>
<td>Rockwell B. 74-78</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>per cent that of copper</td>
</tr>
</tbody>
</table>

The present process of double aging is not limited to the use of a second aging temperature of about 100° C. If the particular copper-chromium-beryllium alloy herein disclosed is precipitation hardend in accordance with prior art practice and thereafter cold worked to effect a desired condition of strain, for example by a cold reduction of about 35 or 50% it may be aged thereafter at any temperature from about 100° C. to 500° C. without loss in hardness or change in its micro structure even when subjected to a stress of 5000 pounds per square inch at 500° C. for 4000 hours. Aaging in this range results in an increase in elongation up to 20% and an increase in electrical conductivity up to 75% with no changes in other properties as noted.

The maximum upper temperature which may be employed in the second aging step may be determined readily by trial heating at various temperatures. Ordinarily, there is no change in hardness up to the temperature of the first precipitation hardening step. A sharp decline in hardness of the alloy, obtained by heating the alloy at some temperature above the temperature of the first precipitation hardening step, indicates that recrystallization has taken place in the alloy. In the copper-chrome-beryllium alloy a decline in hardness is obtained at a temperature of about 450° C. indicating the beginning of recrystallization at this temperature. The maximum service temperature for double aged copper base alloys treated in accordance with the present process is substantially the critical precipitation temperature, for example in the copper-chrome-beryllium alloy disclosed herein, about 500° C. I have illustrated my invention in connection with copper-chrome-beryllium alloys, but, as hereinbefore set forth, it is not limited to such alloys and may be applied to any copper base precipitation hardenable alloy. However, the improvement which may be obtained in some of these alloys may not be of such a degree as to warrant the added cost of the present treatment.

The following is a partial list of alloys which, when subjected to the double aging process hereinbefore disclosed all show improvement in physical properties over those obtained by means of a simple precipitation hardening process. This list is not complete but merely representative. Also, it will be understood that the present process is not limited to alloys which have the exact percentages of ingredients recited in these examples:

1. 0.9% Cr, remainder Cu
2. 0.9% Cr, 1% Co, remainder Cu
3. 3.5% Fe, 3.6% Co, remainder Cu
4. 2.3% Ag, 1.2% Co, remainder Cu
5. 2.5% Cd, 1.2% Co, remainder Cu
6. 3.5% Fe, 7.2% Co, remainder Cu
7. 2.5% Cd, 2.5% Co, remainder Cu
8. 0.1% Be, 0.4% Cr, remainder Cu
9. 0.1% to 3% Sn, 0.1% to 3% Co, remainder Cu
10. 0.2% to 5% Fe, 0.2% to 7% Co, remainder Cu
11. 3.5% Fe, remainder Cu
12. 2.3% Ag, remainder Cu
13. 4.6% Ti, remainder Cu
14. 1% Ti, 1.2% Co, remainder Cu
15. 10% Al, remainder Cu
16. 0.2% to 3% Zr, remainder Cu
17. 3% Zr, 2% Co, remainder Cu

Double aged precipitation hardenable alloys in general yield the unusual combination of high values in elastic limit, proportional limit, elongation, electrical conductivity, resistance to shock and resistance to fatigue and to overloads in fatigue. Tensile strength and hardness do not necessarily show similar increases. Double aging also stabilizes the strain hardening intermediate to the two aging treatments and up to the tem-
perature for critical precipitation. These temperatures are considerably higher than the recrystallization temperatures for cold worked solid solution alloys of similar composition. Thus, double aging effects a useful increase in the service temperature and results in greater stability of useful properties.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. The process for improving the properties of a precipitation hardenable alloy consisting of 0.2% to 3% zirconium with the remainder copper which comprises fully precipitation hardening said alloy, superimposing a condition of strain upon the precipitation hardened alloy and thereafter aging the alloy at a temperature below that which effects any recrystallization in the alloy and below the temperature employed in precipitation hardening said alloy.

2. The process for improving the properties of an alloy consisting of 0.2% to 3% zirconium with the remainder substantially all copper which comprises fully precipitation hardening said alloy, cold working the alloy and thereafter aging the alloy at a temperature below the temperature employed in precipitation hardening said alloy.

RICHARDS H. HARRINGTON.