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METHOD OF TREATING COPPER AND
PRODUCT THEREOF

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The present invention provides for improve-
ments in commercial copper, wherein the recrystallization temperature of the metal has been
raised to such an extent that there is no tendency
of the copper to become detrimentally soft at
such elevated temperatures as are encountered in
soldering operations of the character employed
for example in the soldering of radiators for internal combustion engines.

The copper usually employed in the production
of such radiators contains the relatively high
silver content of from 6 to 8 oz./ton of silver.
The softening temperature of the copper is raised
sufficiently by the addition of silver in the above-
mentioned amounts to enable it to withstand the
temperature of the soldering operations without
softening to a detrimental extent.

In view of the cost of adding silver to copper,
various attempts have been made to produce a
copper which is comparable in its properties, including resistance to softening, to silver-bearing
copper. Among such attempts have been various
efforts to substitute an antimony-bearing copper
for silver-bearing copper, wherein commercial
copper has been alloyed with antimony, but all of
these attempts have been commercially unsuccessful,
the results of such attempts being highly erratic.
These failures have been due, apparently,
to a lack of understanding of the equilibrium
relationship between antimony and antimony
oxide in the copper.

The present invention is based upon certain
discoveries which the inventors have made in
connection with this equilibrium, and in connection
with the behavior of copper when subjected to
certain heat treating operations.

One object of the present invention is to provide
an improved and simplified procedure for
producing a copper which will have a softening
temperature substantially above the temperature
employed in soldering operations, such as, for
example, the soldering employed in radiator
manufacture.

Further objects and advantages of the present
invention will become apparent as the description
proceeds, and the features of novelty are
pointed out in particularity in the appended
claims.

Usual commercial copper, such as that used
in the production of copper cakes, wire bars, and

other commercial forms which are to be subjected
to fabricating operations, are characterized
by a tendency to become soft at relatively low
temperatures, so that fabricated shapes produced
from such copper, such as the fins of internal
combustion engine radiators, are easily distorted
after heating to such temperatures. This softening
is due to recrystallization of the metal.

In accordance with the present invention, it
has been found that commercial copper, such as,
for instance, electrolytic tough pitch copper, when
heated to a temperature within a definite range
and quenched, retains its hardness at temperatures
substantially above those which produce
softening in the untreated copper. That is to
say, by heating commercial copper to a temperature
of from approximately 700° C.—1000° C. and
then quenching the copper in water or in a
pickling solution at room temperatures, the resulting
copper remains hard at temperatures at
which softening of the untreated copper appears.

In case of commercial coppers, this hardening
effect disappears if the copper is annealed during
working. However, this hardening is found
to be permanent if small additions of antimony
be made to the copper prior to its original heating
to the above mentioned temperatures, this effect
being found to be due to the antimony being
held in solid solution after the quenching. The
amount of antimony found to be effective, while
maintaining the conductivity prescribed by A. S.
T. M. standards for electrolytic wire bar coppers
ranges from approximately .003% as the minimum
to approximately 0.02% as the maximum.
This conductivity value is of consequence in that
it is demanded by fabricators, since the thermal
conductivity of the metal approximately follows
the electrical conductivity thereof.

The present improvements are found in practice,
to apply particularly well to the copper
known to the trade as "tough-pitch" copper,
which is used customarily for the production of
cast copper cakes and wire-bars, which copper
contains usually from about 0.025% to about
0.05% of oxygen.

Repeated tests have shown that very markedly
higher softening temperatures are obtained on
either oxygen-free or the above grades of commercial
oxygen-bearing copper in the manner indicated above.

In the case of oxygen-bearing copper, a reaction between antimony and oxygen takes place in the temperature range 500 to 700° C., this reaction, however, resulting in the precipitation of antimony from solid solution as an insoluble oxide, and the loss of its effectiveness in raising the softening temperature. This precipitation apparently takes place in accordance with the reversible reaction



The equilibrium characteristics of this reaction are such that the formation of antimony oxide, Sb_2O_3 , approaches completion at 500° C., and practically all of the antimony may be precipitated at this temperature if sufficient time is allowed for the reaction to take place. As the temperature increases, the amount of Sb_2O_3 that can exist progressively decreases, until at approximately 850° C. practically all of the antimony is present in solid solution. During the hot rolling process, precipitation of Sb_2O_3 occurs as the copper cools from the temperature of the heating furnace. Further precipitation takes place in subsequent annealing between 400 and 700° C.

It is apparent from the equation given above that increases in the amounts of either antimony or Cu_2O present in the copper will increase the amount of Sb_2O_3 formed. The rate of precipitation also increases with increasing amounts of antimony. Additions of antimony to copper for the purpose of raising the softening temperature therefore lose much of their effectiveness after the normal commercial hot rolling and annealing treatments have been carried out.

Since equilibrium conditions in the above equation depend on the temperature, it has been found possible to preserve the antimony in solid solution by heating preferably to approximately 850° C., where Sb_2O_3 cannot exist in appreciable quantities, and then quenching. Carried out on hot rolled material, this process restores the precipitated antimony to its effective form of solid solution, and permits final cold finishing to supply a product having a high softening temperature.

While antimony has been used as an example, and has a large effect on the softening temperature of copper if preserved in solid solution by this heat treatment, the process has also been found to apply to other impurities present in coppers of commercial purity, as has been indicated above. Thus, commercial coppers, both oxygen-bearing and oxygen-free, to which no antimony has been added show a decided increase in softening temperature when heated to 850° C. and quenched, after hot rolling, this effect being obtainable, however, over a range of 700°-1000° C. This is due to the fact that the solid solubilities of certain of these impurities are higher at this temperature; that they are retained in this form of solid solution by the quenching operation, and are therefore rendered effective in raising the softening temperature. This effect is permanent if the metal is not reheated; but the additions of antimony enable the metal to be heated to annealing temperatures during the fabrication process without losing the effect.

Where oxygen-free copper is used, obviously there is no great difficulty in retaining the antimony in solid solution, since the reversible reaction indicated above cannot take place, but nevertheless, an increase of softening tempera-

ture is obtained by the heat treatment due to the increased solubility of other impurities which are present. Quenching is usually done in a pickling solution containing 10% sulphuric acid, and the period of heating necessary to effect the solution is found to be about 20 minutes at 850° C.

As an illustrative example of the results obtained by the present invention, a rod of electrolytic copper containing 0.0068% of antimony was annealed for 20 minutes at 850° C. and quenched, after which the rod was cold drawn to a diameter of 0.162", whereupon it was annealed for one hour at 850° C. and quenched, and cold drawn to 0.081" diameter. It was found that this copper had a softening temperature of 296° C., with a resistivity of .15267 ohm per metergram at 20° C. when annealed for 20 min. at 500° C., whereas silver-bearing copper containing 7.5 oz./ton of silver showed a softening temperature of 295° C. and a resistivity of .15176 ohm per metergram at 20° C. when annealed in the same manner.

The term "softening temperature" as used herein refers to a temperature determined by the following procedure: Samples of the wires are annealed at various temperatures for a period of one hour in an oil bath equipped with automatic temperature control. The tensile strength of the samples is then determined for the hard drawn condition, after anneals at various temperatures in the oil bath, and in the completely annealed condition caused by a one hour anneal at 500° C. Tensile strength is then plotted against annealing temperature, and the point representing 50% of the total drop in tensile strength from the hard drawn to the fully annealed condition is determined, and the temperature corresponding to this point is taken as the softening temperature.

The following table shows comparative softening temperatures after indicated heat treatment.

	Silver-bearing copper (7.5 oz./ton Ag)	Electrolytic wire bar	Electrolytic wire bar + .0068% Sb
Type A (quenched from 850° C.)	295	269	296
Type B (quenched from 850° C. + 1 hr. @ 400° C.)	272	225	270
Type C (quenched from 850° C. + 15 hrs. @ 500° C.)	265	191	215
Type D (quenched from 850° C. + 1 hr. @ 400° C.)			267

The types of heat treatment indicated in the above table are as follows:

Type A: rod annealed for 20 minutes at 850° C. and quenched. Cold drawn to 0.162" diameter and annealed for 1 hour at 850° C. and quenched, then cold drawn to 0.081" diameter.

Type B: rod annealed for 20 minutes at 850° C. and quenched. Cold drawn to 0.162" diameter and annealed for 30 minutes at 400° C. and quenched, then cold drawn to 0.081" diameter.

Type C: rod annealed for 20 minutes at 850° C. and quenched. Cold drawn to 0.162" diameter and annealed for 15 hours at 500° C. and quenched, then cold drawn to 0.081" diameter.

Type D: same as type B, except annealed for 1 hour at 400° C. at 0.162" diameter.

Copper containing 7.5 oz./ton of silver when annealed for 15 hours at 500° C. and quenched before drawing showed a softening temperature of approximately 265° C.; when annealed for 1 hour at 850° C. and quenched before drawing, it

showed a softening temperature of 295° C., the softening temperature of the silver-bearing copper being increased, therefore 30° C. when subjected to the treatment of the present invention.

When commercial wire bar copper was annealed for 15 hours at 500° C. and quenched before drawing, it showed a softening temperature of 191° C.; and when annealed 1 hour at 850° C. and quenched before drawing, it showed a softening temperature of 269° C., or an increase of 78° in its softening temperature when subjected to the present process.

Upon the addition of 0.0068% antimony to the above wire bar copper, and the material annealed for 15 hours at 500° C. and quenched before drawing, it showed a softening temperature of 215° C.; but when the same copper was annealed for 1 hour at 850° C. and quenched before drawing, it showed a softening temperature of 296° C., or an increase of 81° C. in the softening temperature. It will be seen that the softening temperature of this copper when annealed at 850° C. and quenched before drawing is substantially the same as that of the copper containing 7.5 oz./ton of silver when subjected to the same annealing and quenching treatments.

From the foregoing considerations, it will be seen that the present procedure raises the softening temperature of even silver-bearing copper. The increase in its softening temperature apparently is independent of the silver content, which in the amounts present is completely soluble at both 500° C. and 850° C. The noted rise in softening temperature is believed to be due to increases in the solubilities of other impurities in the copper at 850° C.

In the case of electrolytic wire bar, which showed an increase of 78° C. when subjected to the treatment of the present invention, it is believed that the change is due also to increased solubility of impurities at 850° C. Likewise, the electrolytic copper to which a small amount of antimony was added also has a low softening temperature if precipitation is allowed to occur at 500° C. Its response to the process of this invention is the largest, it increasing 81° C. in softening temperature.

It is evident from the above data that the softening temperature of each of these grades of copper is dependent not only on chemical composition but also on the heat treatment employed during fabrication. Thus, an addition of 0.0068% antimony to electrolytic wire bar copper is ineffective in raising the softening temperature sufficiently to compare with silver-bearing copper if these coppers are annealed at 500° C. for 15 hours. If the same coppers are annealed for 1 hour at 850° C. and quenched during the fabrication process, and no subsequent anneals are employed during cold fabrication, the softening temperatures are raised to different extents and the electrolytic copper containing 0.0068% antimony is equal in softening temperature to the silver-bearing copper. The softening temperature of electrolytic copper can also be raised substantially by this treatment. It appears that the heating to 850° C. increases the solubilities of the impurities present in these coppers, and quenching from this temperature after solution has occurred retains the impurities in this dissolved condition.

The following table shows comparative ductility of these coppers:

Description	Elongation percent in 10"	
	Heat treatment A ¹	Heat treatment B ²
Silver-bearing Cu (7.5 oz./ton Ag).....	37.5	32.5
Wire bar.....	41.0	35.5
Wire bar+0.0068% Sb.....	41.5	33.75

¹ Heat treatment A.—Wire annealed at 0.162" diameter for 15 hours at 500° C., drawn to 0.081" wire and annealed for 1 hour at 500° C.

² Heat treatment B.—Wire annealed at 0.162" diameter for 1 hour at 850° C. and quenched. Drawn to 0.081" wire and annealed for 1 hour at 850° C. and quenched.

The following table shows the electrical resistivity of electrolytic copper containing antimony, which resistivity was measured in each instance on wires that were annealed for 1 hour at 850° C. and quenched, and then annealed for 20 minutes at 500° C. as prescribed by the A. S. T. M. standards for resistivity measurement.

Percent antimony	Resistivity—ohms per metergram at 20° C.
0.0068.....	.15328
0.0080.....	.15405
0.020.....	.15467

It will be seen, therefore, that the inclusion of a small amount of antimony in accordance with the present invention does not effect deleteriously the ductility of the resulting copper. Also, that the electrical resistivity of the copper containing 0.008% antimony and 0.0068% antimony does not exceed the A. S. T. M. maximum resistivity for high conductivity electrolytic copper wire bars, which is .15436 ohm per metergram, whereas the resistivity of the copper containing 0.020% antimony is but slightly above such standard.

It will be seen from the foregoing description that the scope of this invention includes the obtaining of large increases in the softening temperature of copper by increasing the effectiveness of small amounts of impurities, e. g. antimony, the invention imparting to the copper a softening temperature of above 250° C.

Where high conductivity is of minor importance, such as where the copper is to be used for engraving plates, for example, the antimony content of the copper may be increased to 0.1%.

As it has been indicated in the foregoing, impurities other than antimony have a similar effect. Thus, in determining the effect of impurities varying amounts of sulphur were added both to oxygen-free and to oxygen-bearing copper, the former being very pure copper, and the latter pure except for the oxygen content. The results obtained are tabulated as follows:

Percent S	Percent O	Softening temperature when heated 2 hrs. at 600° C. and quenched	Softening temperature when heated 1 hr. at 850° C. and quenched
0.....	Nil.....	°C. 136	°C. 136
0.0003.....	Nil.....	163	190
0.0003.....	Saturated ¹	162	185
0.0008.....	Nil.....	174	219
0.0008.....	Saturated ¹	176	206
0.0015.....	Nil.....	176	226
0.0015.....	Saturated ¹	181	234

¹ Saturated with oxygen, i. e. the copper contained enough oxygen to saturate the solid solution of oxygen in copper at 850° C.

It will also be noted from the foregoing that the process of quenching from 850° C. when applied to pure copper to which .0015% sulphur has been added, raises the softening temperature 90° C. as compared to pure copper containing no sulphur. The same copper heated to 600° C. and quenched, showed but a 40° C. increase in softening temperature. It will also be seen that the pure copper being free from detectable amounts of all impurities is entirely unaffected by quenching from 850° C. This will be apparent from the previous description of the process, which requires the presence of impurities in order that they may be converted into solid solution within the temperature range of 700–1000° C. before they are retained in this condition by the quenching operation.

In addition, it will be seen from the data that the addition of oxygen to the coppers containing various amounts of sulphur had no effect on the results of the quenching treatment from 850° C. which produced substantial increases in the softening temperatures of the various coppers, irrespective of the presence or absence of oxygen as described previously herein.

What is claimed is:

1. The process of treating copper containing from 0.025% to 0.05% oxygen for increasing the softening temperature thereof, which comprises including antimony therein in effective amounts but not exceeding substantially 0.02% thereof, heating the said copper to within a temperature range of from approximately 700° C. to approximately 1000° C., maintaining the said copper within such temperature range until the antimony is converted substantially completely into solid solution in the copper, and quenching the resulting copper from the said temperature to maintain the antimony in solid solution.

2. The process of treating commercial oxygen-bearing copper containing 0.025% to 0.05% oxygen for increasing its softening temperature, which comprises alloying with the said copper

from approximately 0.003% to approximately 0.02% of antimony, heating the resulting copper to a temperature not less than substantially 850° C., maintaining the said temperature until substantially all of the antimony has been converted into solid solution in the copper, and quenching the resulting heat-treated copper from the said temperature to maintain the antimony in solid solution.

3. The process of treating commercial tough-pitch copper containing from 0.025% to 0.05% oxygen to increase its softening temperature, which comprises heat-treating the copper at temperatures ranging from substantially 700° C. to substantially 1000° C. until impurities including antimony are converted substantially completely into solid solution in the copper, and quenching the copper from such temperatures to maintain such impurities completely in solid solution.

4. A new metallurgical product composed of commercial tough-pitch copper containing antimony but not more than approximately 0.02% thereof, the antimony being substantially entirely in solid solution in the copper in the presence of from 0.025% to 0.05% oxygen contained in the copper.

5. A new metallurgical product composed of commercial oxygen-bearing copper containing from approximately 0.025% to approximately 0.05% oxygen, and from approximately 0.003% to approximately 0.02% of antimony which is present at least substantially entirely in solid solution.

6. As a new metallurgical product, heat-treated copper having impurities including antimony present substantially completely as solid solution in the copper, the said copper having a composition corresponding substantially to commercial tough-pitch copper but having a softening temperature substantially above 250° C.

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