

- [54] WIRE PRODUCT AND METHOD OF MANUFACTURE
- [75] Inventors: **Yoshio Matsuda; Yoshio Maeda,**
both of Osaka, Japan
- [73] Assignee: **Sumitomo Electric Industries, Ltd.,**
Osaka, Japan
- [22] Filed: **Aug. 15, 1972**
- [21] Appl. No.: **280,813**
- Related U.S. Application Data**
- [63] Continuation-in-part of Ser. No. 879,102, Nov. 24, 1969, abandoned.
- [52] U.S. Cl. **148/12.7**
- [51] Int. Cl. **C22f 1/08**
- [58] Field of Search **148/11.5 R, 12.7**
- [56] **References Cited**
- UNITED STATES PATENTS**
- | | | | |
|-----------|--------|--------------|--------|
| 2,049,500 | 8/1936 | Hensel | 75/153 |
| 2,148,151 | 2/1939 | Darby | 75/153 |

3,172,762 3/1965 Wilson..... 75/153

Primary Examiner—W. Stallard
Attorney, Agent, or Firm—Carothers and Carothers

[57] **ABSTRACT**

A wire product and method of manufacture particularly adaptable for wire wrapping termination wherein wiring conductors are wrapped around connection terminals of electrical and electronic machines and appliances. The wire product is made from a four-element alloy comprising mostly copper and the remainder cadmium, silver and chromium which is first subjected to a solution heat treatment consecutively followed by rapid cooling, cold working to produce a fine wire and aging treatment. The wire product made within the confines of the present invention will produce a wire that has high releasing force from a terminal connection in excess of EIA standards and low electric contact resistance.

2 Claims, 11 Drawing Figures

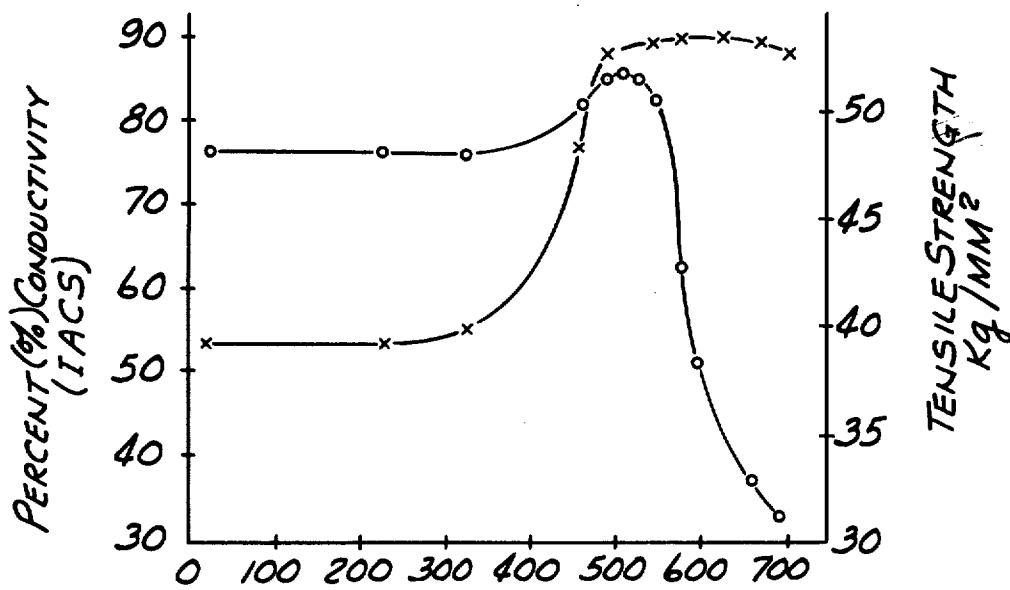


Fig. 1

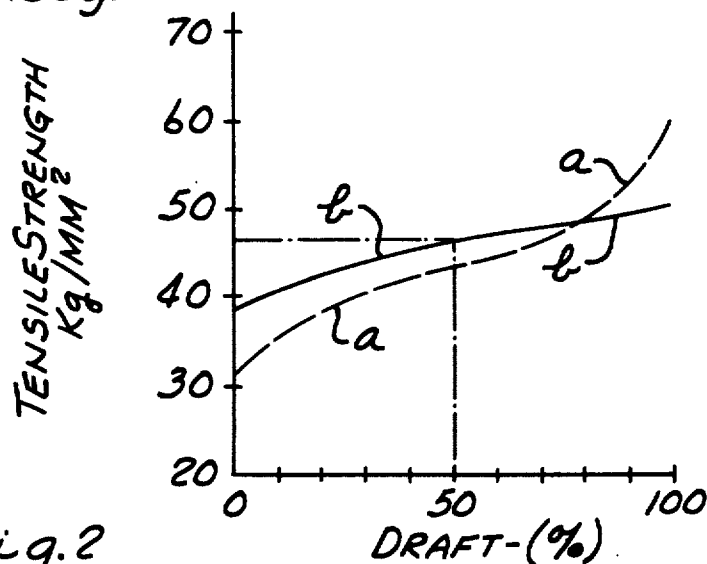


Fig. 2

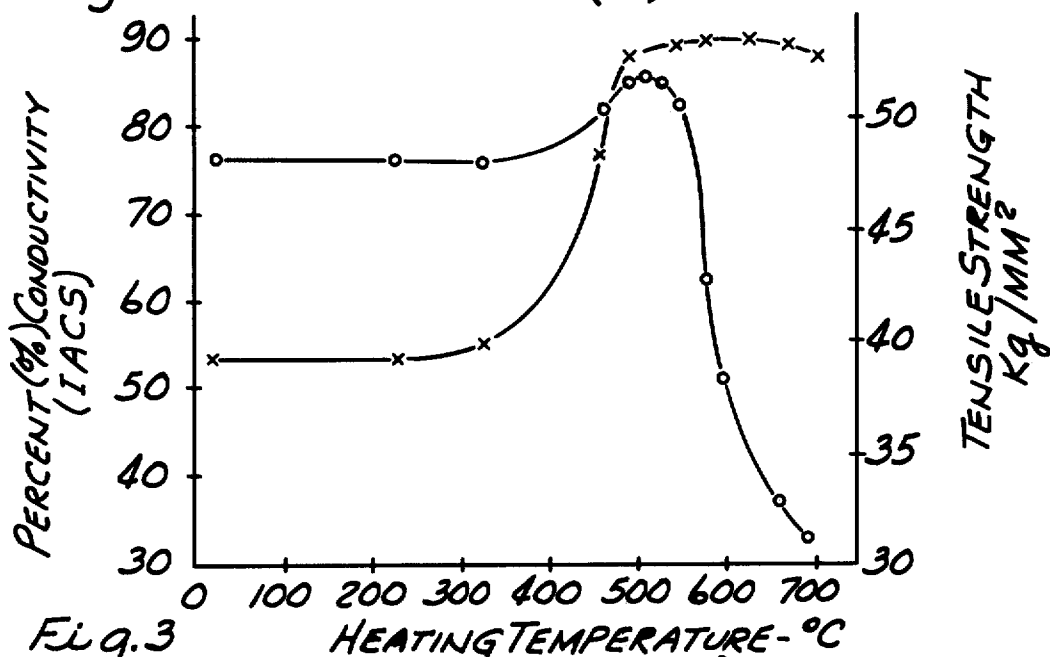


Fig. 3

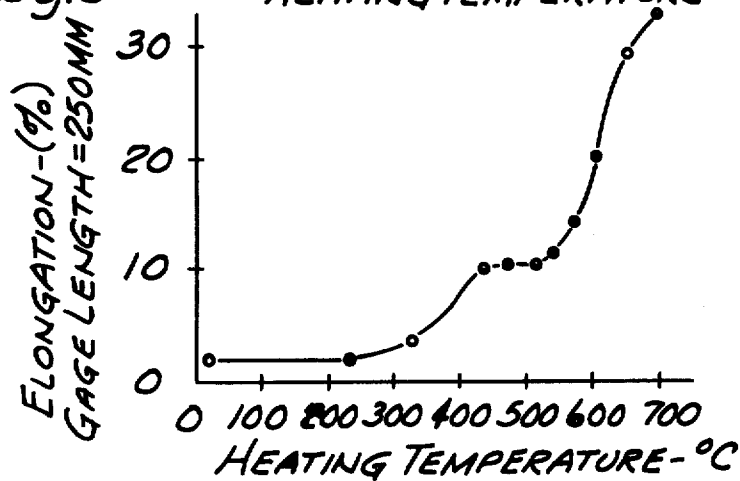


Fig. 4

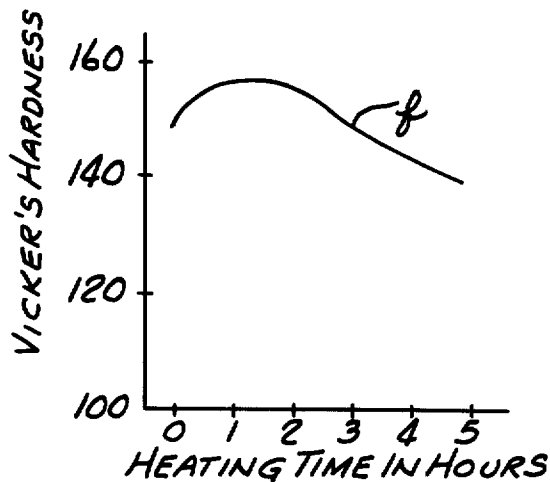


Fig. 5

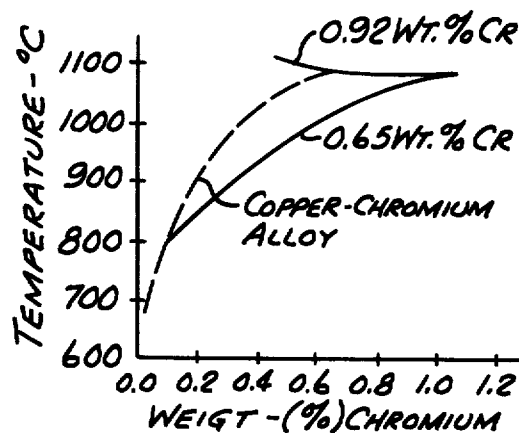


Fig. 6

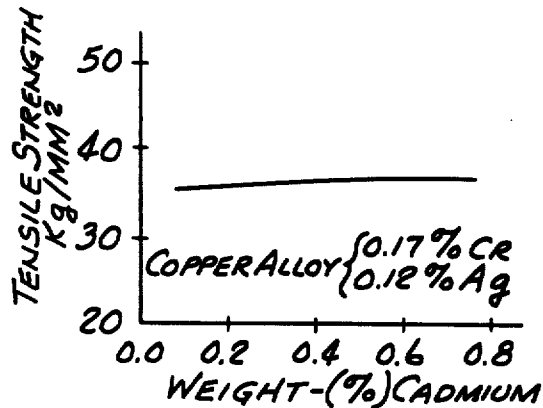


Fig. 7

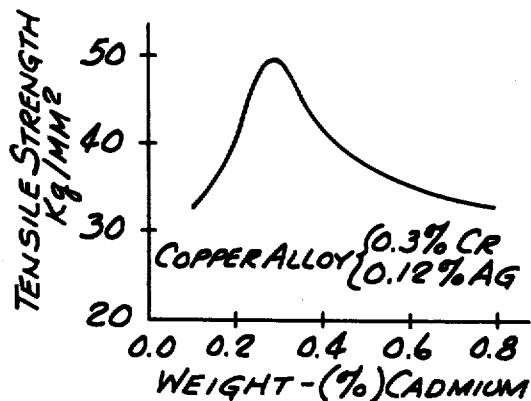


Fig. 8

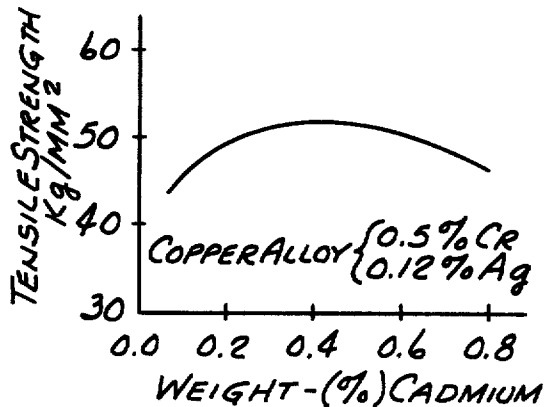


Fig. 9

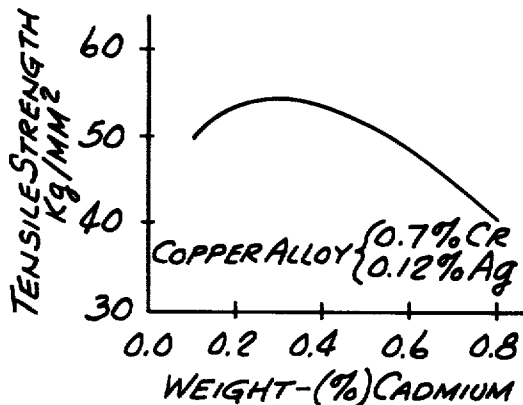


Fig. 10

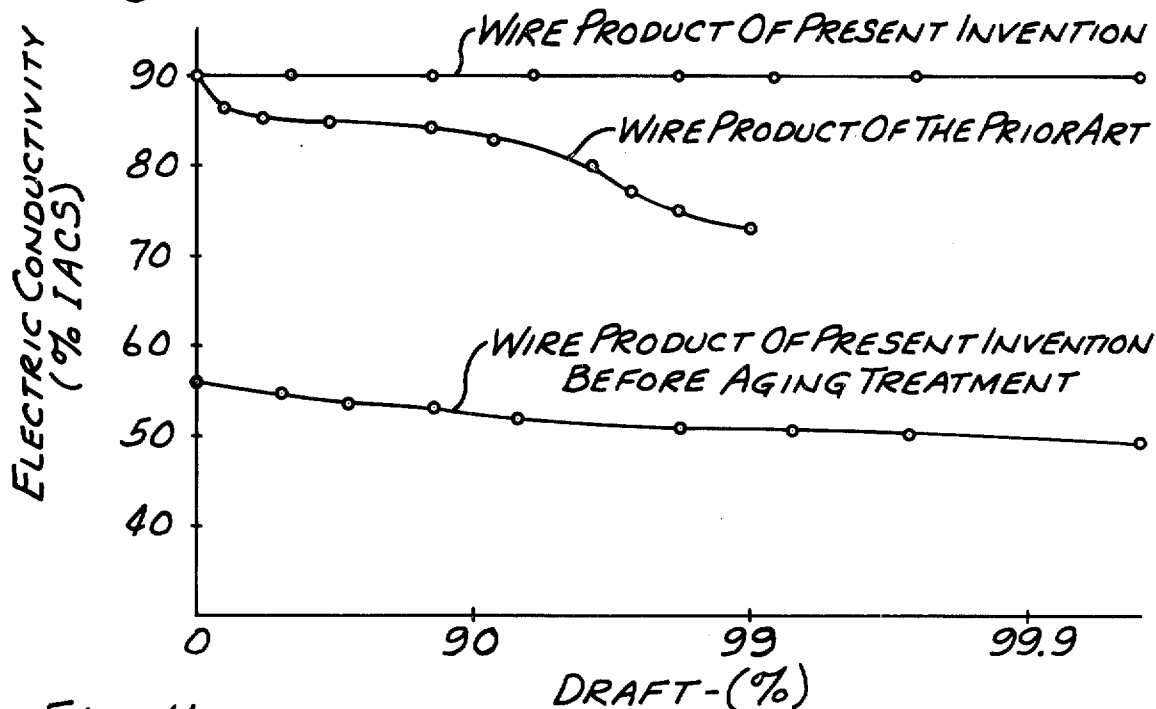
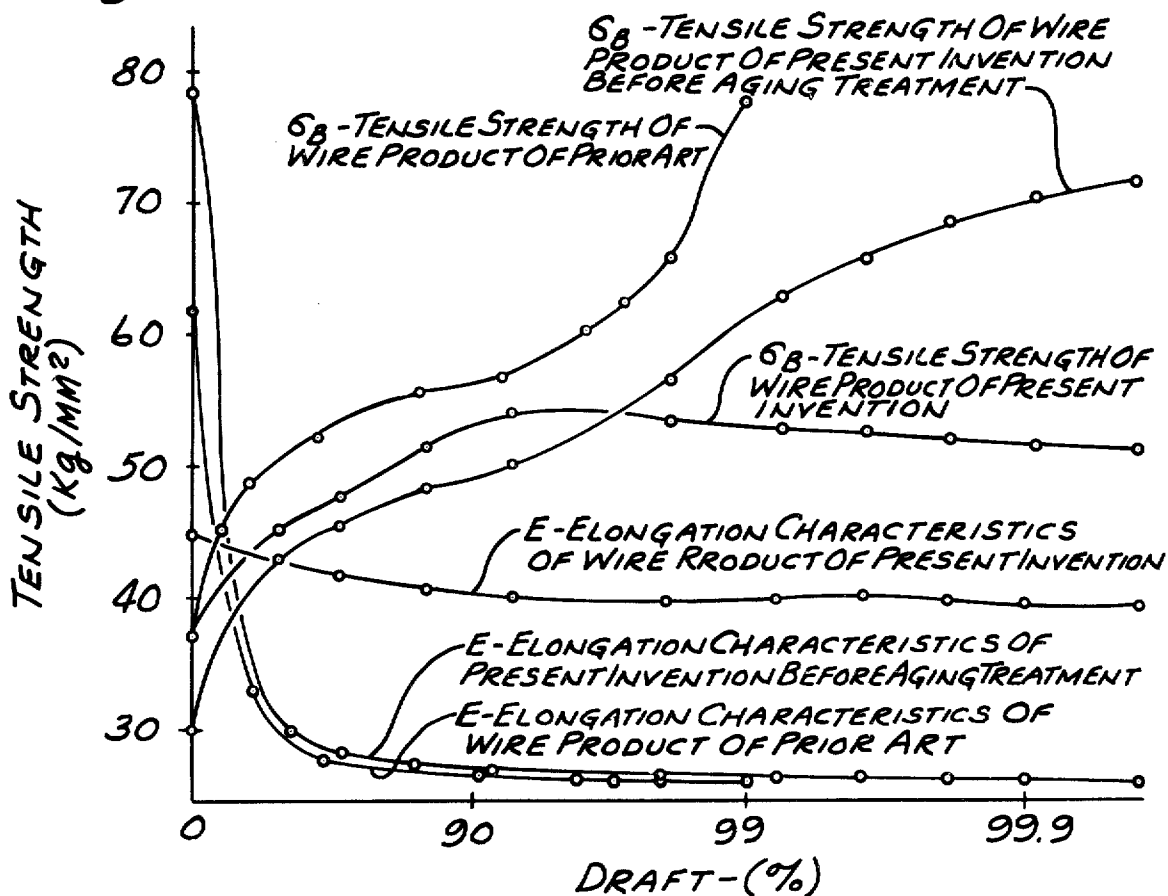


Fig. 11



WIRE PRODUCT AND METHOD OF MANUFACTURE

CROSS REFERENCE TO RELATED PATENT APPLICATION

This is a continuation-in-part of patent application Ser. No. 879,102 filed Nov. 24, 1969, and now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a wire product and a method of manufacturing the same from a copper-base alloy.

With regard to copper alloys for electric conductors heretofore in use, there are copper-base alloys made by adding silver or chromium as a second element to pure copper or oxygen-free copper and processing it for strain hardening, and copper-base alloys made by adding chromium, zirconium, etc., to such copper and giving it processing and heat treatment for precipitation hardening. However, any and all of these alloys have both merits and demerits with respect to their properties, such as strength, heat-resistance, elongation, flexibility, thermal and electrical conductivity, etc., so that they cannot be said to be electroconductive materials which are satisfactory in all respects.

The alloys of copper containing silver or cadmium are known in the prior art to have a great strength, but are inferior to alloys of the heat treatment type with respect to flexibility, heat-resistance, and elongation. The alloys of copper containing cadmium, chromium or zirconium are satisfactory with respect to the above-mentioned properties if compared with worked-on alloys, but do not possess satisfactory properties to meet various practical requirements for wires, such as the requirements that have to be met when employed on peg wire terminals in electric machines and appliances. In this connection, reference is made to U.S. Pat. No. 3,172,762 (75-153) which is directed to a copper-base alloy containing chromium and cadmium in the proportions claimed to produce a wire product having high mechanical strength and electrical conductivity even after exposure to high temperatures in electrical wire installations in machines and appliances. However, it has been discovered by us that if the addition of silver is made to such an alloy in accordance with the method disclosed and claimed herein, a wire product is produced having better adaptability for post or peg connection such as found on wiring boards in computers, in that the wire has much higher releasing force because of its better "gripping" ability on such peg terminals due to its improved mechanical properties as well as having low electrical contact resistance. The addition of silver improves the wire characteristics for wire wrapping connections and it is believed that the small addition of silver has the effect of increasing the solubility limit of chromium in copper, as well as bringing about a more uniform distribution of the cadmium in copper due to the affinity of silver for both copper and cadmium. Also, the addition of the silver improves the tensile strength as compared to the prior art copper-base wire products.

Alloys of high reliability which offer no difficulty in connecting and bending are now in high demand especially for parts of such electronic machines and appliances as electronic computers, electronic exchange, etc., and for wirings in and between such machines and appliances. None of the copper alloys heretofore in use

are, however, of a reliability which is entirely satisfactory.

Generally speaking, when wiring is made in such an electronic machine or appliance as an electronic computer, electronic exchange, etc., a technique is employed in which electric connection is effected by wrapping the wiring conductor around the connecting terminal conductor with a wrapping force applied thereto. In order to have the wiring conductor squeeze itself into the connecting terminal conductor to decrease the electric contact resistance between the two, it is required that the wiring conductor have great strength and great local elongation; it is also required that it have conductivity of 85 percent or more in order to have a large current capacity.

In view of what has been mentioned, this invention aims at the method of treating and cold working a copper-base alloy for electrical conduction whose properties fully satisfy the requirements of strength, heat-resistance, elongation, flexibility and thermal and electrical conductivity, releasing force required by EIA standards (Electronic Industries Association Standards), and is characterized by four-element alloys consisting of copper, cadmium, silver and chromium.

This four-element alloy is disclosed in U.S. Pat. No. 2,049,500 but not in the same quantities of composition as herein disclosed nor is the method employed in this Patent the same as herein disclosed, as we have found that the elements should be added in a named order. Further, U.S. Pat. No. 2,049,500 does not provide an alloy for a wire product having going wire wrapping characteristics and, in fact, is directed to the production of castings. U.S. Pat. No. 2,049,500 further requires an intermediate heat treatment prior to a cold working which cannot be employed in the method herein disclosed. For better understanding of the nature of the method of manufacture of the present disclosure, reference will be made later on a comparative basis between the methods of this disclosure and that of U.S. Pat. No. 2,049,500.

SUMMARY OF THE INVENTION

This invention relates to a method of manufacturing heat-resistant copper alloys for electric conductors which is characterized in that a four-element alloy consisting of cadmium, silver, chromium and copper making up the remainder of the alloy is subjected to solution heat treatment for 0.5 - 2 hours at a temperature of 900°C - 1000°C and is then rapidly cooled for cold working to give it a cold draft of 50 percent or more. An aging treatment is thereafter applied to prevent gradual precipitation hardening. Wiring conductors made by the method of this invention satisfy the aforementioned requirements which have not been satisfied by the electric wires and conductors which have heretofore been made known to the public. The copper-base alloy, if made into wire in accordance with the disclosure, provides for a wire of high ductility adaptable for wire wrapping connections and yet having all the other wire properties desirable in good electrical wires such as high conductivity, tensile strength and excellent elongation properties.

The copper alloy composition of the wire product disclosed is a four-element alloy consisting of

- 0.2 - 0.5 wt-percent cadmium
- 0.03 - 0.2 wt-percent silver
- 0.2 - 0.7 wt-percent chromium

with the balance made up of copper. The method of manufacturing the alloy and for production of the wire is very important in order to obtain a wire highly desirable for wire wrapping installation because of its high ductility, tensile and yield strength, and electrical conductivity after aging.

Briefly, the four-element alloy as defined by the above set forth ranges is believed to be highly successful for wire wrapping connections for some of the following reasons.

The silver added to the alloy in the quantity range of 0.03 to 0.2 wt-percent has the effect of increasing the solid-solubility limit of chromium in copper from 0.65 wt-percent to as high as 0.92 wt-percent. As a consequence, the content of chromium can be increased by the addition of silver thereby effectively increasing the adaptability of the alloy for heat treatment hardening. Like cadmium, silver itself has an action to strengthen the copper matrix and increase the tensile strength of the wire produced from the alloy without lowering its ductility.

It is known that it is very difficult to obtain a uniform solid solution of cadmium in a copper alloy. However, if cadmium and silver are added simultaneously, a uniform distribution of cadmium in copper is obtained and the copper alloy is overall strengthened because silver has good affinity for both copper and cadmium.

The surprising result of following precisely the method of manufacturing of wires with the copper-base alloy disclosed is the excellent resistance to release from a wire terminal connection. The EIA standards specify that for wire diameters of 0.511 mm, 0.405 mm and 0.254 mm, the releasing force necessary to remove the wrapped wire from a terminal peg should respectively be 2.95 kg or more, 2.27 kg or more, and 1.40 kg or more. The employment of the alloy and method as taught in this disclosure has shown on the average that for a 0.254 mm diameter wire, the releasing force is 9 kg and for a 0.455 mm diameter wire, the releasing force is 6.5 kg. These values exceed to a great extent the EIA imposed standards.

Other objects and advantages appear hereinafter in the following description and claims.

The accompanying drawings show, for the purpose of exemplification, without limiting the invention or the claims thereto, certain practical embodiments illustrating the principles of this invention wherein:

FIG. 1 illustrates the relationship between the cold draft given by the manufacturing method of this invention and the tensile strength obtained as a result.

FIG. 2 illustrates the relationship between the heating temperature of the aging treatment in accordance with the manufacturing method of this invention and the resultant tensile strength and electroconductivity.

FIG. 3 illustrates the relationship between the temperature of the aging treatment and the elongation of the alloy obtained.

FIG. 4 illustrates the relationship between the length of time of the aging treatment and the hardness.

FIG. 5 is a metallographic illustration of copper chromium alloy.

FIGS. 6 through 9 graphically illustrate the variations in tensile strength for varying amounts of cadmium in the alloys of this invention. In FIGS. 6 through 9, the silver content is the same, but in FIG. 6, the chromium content is 0.17 wt-percent; in FIG. 7, 0.3 wt-percent; in FIG. 8, 0.5 wt-percent and in FIG. 9, 0.7 wt-percent.

FIG. 10 is a graphic illustration of the relationship of draft and electrical conductivity between the wire product made in accordance with the alloy and method herein disclosed as compared to a wire product made from the alloy and method of U.S. Pat. No. 2,049,500.

FIG. 11 is a graphic illustration of the relationship of draft, tensile strength and elongation between a wire product made in accordance with the alloy and method herein disclosed as compared to a wire product made from the alloy and method of U.S. Pat. No. 2,049,500.

The manufacturing processes of this invention are not radically different from the manufacturing processes of the alloys of the ordinary heat treatment type. With respect to the processing conditions in individual processes, however, there are specifically fixed allowable ranges which must be maintained. Only where such conditions are satisfied, the wire product of this invention will be obtained in accordance with the method of manufacture disclosed and claimed.

First, as copper for use in this invention, both phosphor deoxidized copper and oxygen-free copper may be used. Cadmium and chromium, as additional elements in the copper-base alloy, products of commercial purity are sufficient, and it is preferable to add them in the form of a mother alloy. For example, mother alloys, such as Cu - 5-15 wt-percent Cr, or Cu - 50 wt-percent Cd, or the like, may be used. Silver is added in the form of a single element. The sequence of adding is this: Chromium is added to molten copper prepared by heating oxygen-free copper to 1200°C - 1300°C to make a chromium-copper alloy, and then silver and cadmium are added in the named order. If this named order of additions is not observed, the four-element alloy of the prescribed constitution cannot be properly obtained to produce a wire product having the desired characteristics as previously discussed.

The alloy as constituted is placed into a water cooled copper mold or the like, and is then heat processed, being heated to a temperature of 800°C - 900°C. What is meant by heat processing here has reference to rolling and extrusion at a high temperature. Both techniques produce favorable workability, but temperatures exceeding 800°C are not favorable because cracking would take place when rolling is done at such high temperatures, while cracking due to gross crystal grains would take place at temperatures above 980°C.

The alloy is then subjected to a solution heat treatment for 0.5 - 2 hours at 900°C - 1000°C. The reason why the solution heat treatment is restricted to these conditions is to prevent uneven precipitation of chromium. In order to effect solid solution of chromium as far as possible, at least 30 minutes within the temperature range of 900°C - 1000°C is necessary. If the length of time exceeds 2 hours, however, it is not favorable because the crystals become gross and large, although there is no difference in the solid solution effect.

After the solution heat treatment is over, cooling is effected rapidly in order to maintain at room temperature the solid solution state of chromium obtained by the solution heat treatment.

Rapid cooling may be effected by methods already well known, such as quenching. Unless rapid cooling is done, the rate of precipitation aging, which will be discussed later, becomes low.

After the cooling, cold processing of the copper alloy is accomplished always before the aging treatment. It is preferable to give a cold draft of 50 percent or more.

The reason why the cold draft is made 50 percent or more is that it is desirable to make the tensile strength of the wiring conductor greater than 46 kg/mm² which is the tensile strength of the hard copper wire heretofore manufactured. The tensile strength of the wire product is influenced at that point in the manufacturing process wherein the aging treatment is accomplished.

The curve (a) and curve (b) of FIG. 1 represent the relationship between cold draft and tensile strength of a wire product subjected to solution heat treatment, rapid cooling and thereafter cold worked (curve a), and a wire product subjected to solution heat treatment, rapid cooling, cold working and then aging treated (curve b), respectively. The copper-base alloy used is that of the present invention. It is clear that transfer from curve (a) to curve (b) is brought about by the aging treatment made after the cold working. It may be seen that from the consideration of tensile strength only, a tensile strength property of a wire product of the present invention similar to that of a hard copper wire upon employing a cold draft of about 40 percent or more, that is, a tensile strength above 45 kg/mm².

The aging treatment made after the cold working is accomplished by a heat treatment for 0.5 - 2.5 hours at a temperature of 450°C - 550°C. This aging treatment temperature is a means for the recovery of electrical properties and the production of the property of elongation, and is at the same time necessary for the improvement of mechanical properties, the precipitation hardening of chromium being added to the strength maintained by cadmium and silver solid-dissolved in the material.

In order to see the effect of this aging treatment, the properties after 1 hour's heating of materials which have been given draft of 50 percent or more are shown in FIG. 2 and FIG. 3. The relationship between the heating temperature and the tensile strength is represented by the curve (d) in FIG. 2, the relationship between the heating temperature of the aging treatment and the specific conductivity by the curve (b), and the relationship between the heating temperature and the elongation for a gauge length of 250 mm by the curve in FIG. 3. From the results of FIGS. 2 and 3, it can readily be seen why the aging temperature preferably does not exceed 550°C.

As can be seen from FIG. 4, a duration of heating which does not exceed 0.5 hour cannot produce the desired hardness, that is, acceptable strength, and elongation. On the other hand, a duration of 2.5 hours or more results in a decrease in hardness as shown by the curve (f). The hardness properties of the wire or conductor after a 1 hour heating is fairly representative of the necessary duration of heat treatment, as shown in FIG. 4, wherein the curve (f) peaks at this point.

While these copper-base alloys are subjected to the cold working and may still be useful even where the aging treatment is not made, the aging treatment is highly desirable where the wire product is subjected for long periods of time at a high temperature when installed in electrical machines and appliances, so as to prevent precipitation hardening from gradually taking place.

The Vickers hardness of the alloy employed in this invention at an aging treatment temperature of 490°C is shown in FIG. 4 for various time lengths of aging treatment and it can be seen that for best results, it is

preferable to carry out the aging treatment within a range of 0.5 - 2.5 hours.

The appropriate ranges of the components making up the copper-base alloy of this invention are 0.2 - 0.5 wt-percent for cadmium, 0.03 - 0.2 wt-percent for silver and 0.2 - 0.7 wt-percent for chromium, as may be seen from a comparison with copper-chromium alloy shown in FIG. 5. Where the chromium content is 0.2 wt-percent or less, the solubility is too small and the electrical properties of the alloy for a wire product are not improved; while where the chromium content is 0.7 wt-percent or more, the maximum solid solution limit is approached and the solution heat treatment becomes difficult to perform. If the solution heat treatment temperature is 1000°C or higher, there is a tendency that the cadmium content of 0.5 wt-percent or more produces crystallization of liquids. This is not at all desirable, because it greatly affects the ability to easily perform any subsequent cold working operation.

FIGS. 6, 7, 8 and 9 are graphs illustrating tensile strength after aging treatment. From a study of these figures, it can be seen that the tensile strength property of the alloy is by no means improved where the cadmium content is 0.2 wt-percent or less of the alloy composition.

Like cadmium, silver is an element which improves the strength of the copper-base alloy, and makes a very important contribution to the alloy make up especially in connection with the property of hardening by cold working. Furthermore, the addition of silver causes the chromium precipitate to take on a fine needle shape, so that it makes it possible to work upon an alloy containing a maximum of 0.7 wt-percent chromium. Especially for providing cold workability of a draft of 50 percent or more, it is necessary to add silver.

The reason why the addition of silver is restricted to 0.03 - 0.2 wt-percent in this invention is that a quantity not exceeding 0.03 wt-percent does not produce the desired tensile strength and elongation, while a quantity not less than 0.2 wt-percent results in a lower unsuitable electrical conductivity.

The electrical and mechanical properties of electric wire or conductor of a diameter of 0.26 mm made of an alloy obtained according to this invention are compared with those of other electric wires having alloy compositions known or in previous use in Table 1. The alloy of this invention shown in Table 1 is one of a 90 percent draft, subjected to aging treatment at 490°C for 1 hour after cold working.

TABLE 1

Alloys	Tensile Strength Kg/mm ²	Elongation at gauge length 250 mm	Electric conductivity (%) IACS	Releasing force from wrapping connection Kg	Electric contact resistance mΩ
Oxygen-free copper	24	24.0	101	5	0.8
Copper-zinc alloy	45	5.4	90	5	0.5
Copper-chromium alloy	46	6.0	80	6	0.4
Alloy of this invention	52	9.2	88	9	0.1

From the above Table 1, it may be seen how great the wrapping force of the alloy of this invention is and how low its electric contact resistance is as compared to copper per se and other copper-base alloys. This adequately shows that the electric wire product of the present invention by squeezing itself upon or being pressed into the terminal conductor or peg for connection therewith has a sufficient strength and adaptability for that particular purpose.

Table 2 shows the experimental values indicating the flexibility of the electric wires of Table 1 (0.26 mm in diameter) bent alternately to 90° under a specific identical load. If the curvature is twice the diameter of the electric wire product when bending to 90° under a load which is 25 percent of the tensile load of the electric wire, it is evident that the wire product of this invention can withstand the most severe conditions.

TABLE 2

Alloys	Bending Values Times
Oxygen-free copper	16
Copper-zirconium alloy	18
Copper-chromium alloy	20
Alloy of this invention	26

In order to more fully understand the method of manufacturing of this application to produce a fine wire product, in particular a wire of 0.018 inch diameter, reference is made to Table 3 and the example identified

TABLE 3

Alloy	Composition wt-%				Tensile Strength Kg/mm ²	Elongation %	Conductivity IACS	Flexibility (times)	Releasing force from wrapping Connection Kg	Electrical contact resistance mΩ
	Cd	Ad	Cr	Cu						
Test I	0.21	0.18	0.58	remainder	53	9	88			
Test II	0.25	0.12	0.50	remainder	51	8.5	89	25	9	0.1
Test III	(0.254 mm)	0.25	0.12	0.50	remainder	56	1.0	84	3	nearly zero
Test IV		0.25	0.12	0.50	remainder	53	8.5	89	26	6.5
Test V	(0.455 mm)	0.25	0.12	0.50	remainder	63	1.0	77	5	nearly zero

as Test I. The copper employed in this test was phosphor deoxidized copper. Cadmium and chromium as additional elements in the copper-base alloy for the wire product may be of ordinary commercial purity. However, it is preferable to add these two elements in the form of another alloy, such as, copper - 5 wt-percent. However, silver is added in the form of a single element.

The sequence for adding these elements is as follows: Chromium is added to molten copper prepared by heating the phosphor deoxidized copper from 1200°C to 1300°C to produce a chromium-copper alloy. Then silver and cadmium are added in the named order. If this named order of additions is not observed, the four-

element alloy of the above-prescribed constitution cannot be properly obtained.

The alloy as formed is then cast into a water cooled copper mold capable of producing an ingot 4½ inches in diameter. The ingot is then heated to a temperature of 800°C to 900°C and thereafter hot-rolled to a wire rod of 5/16 inch diameter. Because of the prescribed constitution of the alloy, the copper alloy as hot-rolled does not contain any cracks and can be rolled very smoothly.

The method for manufacturing the wire product from this wire rod is as follows.

The wire rod is subjected to a solid solution heat treatment at a temperature of 950°C for 1.5 hours. The rod is then quickly cooled in a quenching medium of water.

The wire rod is then subjected to cold working on a continuous drawing machine where it is cold-drawn into a fine wire having a diameter of 0.018 inch. The working reduction through cold drawing in this particular example was 96.8 percent.

The wire, as drawn, was then subjected to a final heat treatment for the purposes of aging to a finished wire product. The aging treatment is a heat treatment at a temperature of 500°C for 1 hour and 40 minutes and, in this case, in an inert atmosphere of nitrogen gas. This aging treatment is important as it recovers the desirable electrical conductivity and elongation characteristics without affecting in a real sense the ductility and tensile strength of the wire product. This is because of the increased addition of chromium bringing about precipitation hardening thereby adding to and maintaining the desired tensile strength in the finished wire product even in face of the original heat treatments performed on the alloy.

The resulting final wire product was tested as to tensile strength, elongation and conductivity and these results are shown in attached Table 3.

The results expressed in Table 3 for Test II and Test III were conducted in connection with a wire having a diameter of 0.254 mm (0.01 inch) respectively manufactured by the manufacturing method as described herein and also by the manufacturing method as described in U.S. Pat. No. 2,049,500, as particularly set forth beginning at Page 1, column 1, line 48 and ending at Page 2, column 1, line 22 thereof. The purpose for comparison of copper alloys having identical composition produced under these different methods is to illustrate that not only is the method disclosed by U.S. Pat.

No. 2,049,500 not the same as the method disclosed herein, but also if followed for the purpose of producing wire highly adaptable for wrapping connections, the desired wire characteristics are not obtained by following the method of that Patent for a wire having the composition as precisely claimed herein. These tests illustrate, therefore, that it is not just the alloy constitution that is important, but rather the method of manufacturing to obtain the finished wire product having the desired characteristics for electrical wiring, particularly where the wire connections are made by wire wrapping on electrical terminals. In this regard, it should be noted that the upper limits of the ranges for cadmium, silver and chromium disclosed in U.S. Pat. No. 2,049,500 are higher than those described in the method of the present application.

Reference is made to Table 3 where the alloy constitution for Tests II and III is shown to be the same. The copper alloy in both cases consists of 0.25 wt-percent cadmium, 0.12 wt-percent silver, 0.50 wt-percent chromium and the remainder is copper. These percentages are well within the limits we prescribed.

In applying the method of the present invention in Test II in Table 3, the step of solution heat treatment after hot rolling of the formed alloy to a rod diameter of 8 mm, was carried out at a temperature of 960°C for 1.5 hours. The rod as heat treated was quenched and thereafter cold drawn to a diameter of 0.254 mm. The wire product then received a final treatment for 1 hour at 450°C. The results of Test II are shown in Table 3 including the wire flexibility characteristic as a means to show durability measured by the number of times the wire may be bent at a single point before it breaks.

In applying the method of U.S. Pat. No. 2,049,500, as disclosed on Page 1, column 2, and at the top of column 1 on Page 3, Test III, the solution heat treatment of the 8 mm. diameter rod was also carried out at 960°C for 1.5 hours. This is within the prescribed range of 600°C to 1000°C, indicated preferably above 700°C. The rod was then rapidly cooled by quenching. Then the aging treatment was applied for one hour at 450°C, which temperature is within the range of 350°C to 600°C prescribed at the top of column 2 on Page 2 of U.S. Pat. No. 2,049,500.

Cold drawing was then carried out, but drawing was difficult at a diameter of 0.8 mm so that aging treatment was again carried out for one hour at 450°C, after which cold drawing was accomplished to a diameter of 0.254 mm. The properties of the final wire product thus produced are shown in Table 3 under Test III. It should be noted that flexibility of Test II is more than eight times that of Test III. Note further that conductivity is relatively higher. There is no comparison as to releasing force, as the wire of Test III would not hold at all under a pulling force, while the wire product of the present invention held to 9 kg., far in excess of EIA standards.

Test IV was the employment of the same alloy following the method of the present application but where the final wire product during the cold drawing step was cold drawn to 0.455 mm. Test V was the employment of the same alloy following the method of U.S. Pat. No. 2,049,500 as in the case of Test II, but where the final wire product during the cold drawing step was also cold drawn to 0.455 mm as in the case of Test III.

Before further referring to any of the results from Tests II through V, it should be noted that in following

the method of U.S. Pat. No. 2,049,500, the initial solution heat treatment has been conducted at 1.5 hours, rather than in the range prescribed therein, that is, 10 to 30 minutes. Such a short duration of time is not sufficient heating, since this heating period is too short so that the central portion of the wire rod does not reach the temperature of 960°C, or if it does, it is maintained at that temperature for a short duration. Thus, the solid solution treatment of the alloy components is not effected thoroughly enough so that the final wire product has a lower tensile strength. For example, portions of the 8 mm diameter rod of Test V were treated within the time interval defined by the method of U.S. Pat. No. 2,049,500, wherein solution heat treatment was conducted at 960°C in one case for 10 minutes and in a second case at 960°C for 30 minutes. As a result, the tensile strength in the case of the 10 minute duration heating time was 55 kg/mm², and in the case of the 30 minute duration was 62 kg/mm². The electrical conductivity in the case of the 10 minute duration was 80 percent, whereas in the case of the 30 minute duration it was 77 percent. Upon examination of Table 3 with regard to the results for Test V, it will be seen that the tensile strength is improved where the solution heat treatment period of time is 1.5 hours without any further decrease in the percentage of electrical conductivity level. From these results, it can be seen that the period of time for solution heat treatment from 0.5 to 2 hours prescribed for in the method herein defined and claimed is quite appropriate as a condition for the solution heat treatment.

From Table 3, it can be seen that the wire products of Tests I, II and IV are superior to those of Tests III and V, and this has been found to be particularly true where these wires are cold drawn to diameters less than 1.0 mm. Also, it should be noted the differences obtained in Tests II and IV as compared to Tests III and V with regard to wire flexibility wherein, for example, the wire of Test II could withstand flexures up to 25 times whereas the wire of Test III broke after only 3 flexures, and the wire of Test IV could withstand 26 flexures, whereas the wire of Test V failed after 5 flexures. Further, it should be noted upon examination of the releasing force from wrapping connections measured in kilograms, the releasing force of the wire of the present invention is quite extensive as compared to any releasing force provided by the wire manufactured in accordance with the U.S. Pat. No. 2,049,500 method. In the case of the wire product made according to this Patent, the releasing force is nearly zero. It should be noted that the releasing force is where the specimen wire is taken and wound eight turns around a bronze terminal post which in this particular case was 0.8 mm square in cross-sectional area. The force to pull the wire off the post is measured to determine the strength of the connection made. It is quite evident from the results shown in Table 3, that the wire products made from following the method of U.S. Pat. No. 2,049,500 have practically no engaging strength at all on such terminal posts used frequently today in the electrical and electronic industry.

Also, mention should be made of the electrical contact resistance as measured in millimeters-ohms. In this connection, it will be noted that the contact resistance is less with respect to the wire product made from the method herein disclosed and claimed as compared

to the wire made by following the method disclosed in U.S. Pat. No. 2,049,500.

The foregoing reveals that the wires produced by the method of U.S. Pat. No. 2,049,500 have no adaptability and, therefore, desirability for wire wrapping termination which is the important and desired function of the wire product of the present invention.

In order to demonstrate the importance of the upper limits of the metal constituents making up the wire product used in practicing the method, further tests, Tests VI and VII, were conducted as follows. The alloy of Test VI contains constituents near the upper limits as defined in the specification of the application. In the case of Test VI, the constituents were 0.70 wt-percent chromium, 0.15 wt-percent silver, 0.45 wt-percent cadmium, and the remainder copper. In the case of Test VII, the alloy constituents were 0.75 wt-percent chromium, 0.50 wt-percent silver, 0.90 wt-percent cadmium, and the remainder copper. It will be noted upon examination of U.S. Pat. No. 2,049,500, particularly at the bottom of the first column on Page 1, as well as an examination of, for example, claim 2, these latter constituents constitute the near upper limits as designated.

In connection with the alloy of Test VI, the alloy was first melted and cast into an ingot having a diameter of 100 mm and a length of 1,500 mm. Then the ingot was heated to approximately 900°C and rolled to a wire rod through the use of a hot rolling machine and was rolled to a diameter of 8 mm. During this rolling, no cracks occurred on the surface of the wire rod of Test VI, and a good wire rod was obtained. In the case of the alloy of Test VII, however, when the hot rolling was conducted to produce a wire rod of 8 mm, a series of cracks occurred in the surface of the wire rod after the hot rolling operation.

The wire rod of 8 mm diameter of Test VI was then given a solution heat treatment at 960°C for 1.5 hours and, after rapid cooling, was cold drawn to a diameter of 0.455 mm. Then aging treatment was effected at 450°C for 1 hour. The electrical conductivity level (IACS percent) of this wire was found to be 84 percent.

The wire rod of 8 mm diameter of Test VII was tested according to the teachings of the present invention. A section of the wire rod was picked that was comparatively free from surface cracks as compared to the other portions of the same rod and this section was taken and given a solution heat treatment at 960°C for 30 minutes. After rapid cooling, an aging treatment was performed at 450° C for 1 hour and then the wire rod was cold drawn to a diameter of only 7 mm, being only a draft of 23 percent. A greater draft was not performed on the wire rod because drawing the wire rod to a smaller size was impossible on account of the development of surface cracks in the wire produced. The electrical conductivity level (IACS percent) of this 7 mm diameter wire was 78 percent.

From the foregoing, it can be readily seen that where an alloy within the upper limits of the constituents defined by U.S. Pat. No. 2,049,500 is employed and is compared to an alloy made from the constituents within the upper limits disclosed herein, there is difficulty in obtaining good workability of the alloy particularly in the cold drawing operation to produce a fine wire and also the conductivity level is under 80 percent, which is not very satisfactory wherein the fine wire is going to be employed in wiring installations, particularly where a large current capacity is necessary. In

such cases, the conductivity level should be at least 80 percent or more.

Reference is now made to two graphic illustrations identified as FIG. 10 and FIG. 11, wherein there is shown the various properties such as electrical conductivity, tensile strength and elongation measured at various diameters of wire products produced from the copper-base alloy as manufactured in accordance with the method herein disclosed in comparison with the method taught in U.S. Pat. No. 2,049,500. The copper-base alloy employed consisted of 0.25 wt-percent cadmium, 0.12 wt-percent silver, 0.50 wt-percent chromium and the balance copper. The results in FIGS. 10 and 11 may be identified in particular by "wire product of present invention before aging treatment;" "wire product of the present invention," of course, after the aging treatment; and "wire product of the prior art," which is made in accordance with U.S. Pat. No. 2,049,500.

In following the method described herein, solution heat treatment was made to the alloy which had been hot rolled to a diameter of 8 mm for 1.5 hours at 960°C. Then after rapid cooling, the alloy was cold drawn to various diameters as indicated by the percent draft both in FIGS. 10 and 11. Thereafter, the final wire product was age treated. In each case in FIGS. 10 and 11, where information is designated as "before aging," the final aging treatment was not made in accordance with the present invention to illustrate the importance of aging to produce the wire of the present invention having the desirable electrical characteristics particularly in connection with wire wrapping installation. Thereafter, aging treatment was conducted for that particular wire and the information as shown in FIGS. 10 and 11 designated as "wire product of present invention."

In connection with the test results of "wire product of prior art," the process of U.S. Pat. No. 2,049,500 was followed. Solution heat treatment was made at a diameter of 8 mm of the alloy, thus produced, for 1.5 hours at 960°C. Then after rapid cooling, aging treatment was made for one hour at 450°C. Then the product was cold drawn to the prescribed sizes indicated by the percent draft in connection with information designated as the prior art wire as shown in FIGS. 10 and 11.

From the results shown in FIG. 10, it can be seen that the fine wire product produced by the method of the present invention has a low electrical conductivity before aging but shows a remarkable improvement in conductivity upon final aging treatment in that aging brings about an increase in electrical conductivity of almost two times that of the alloy before aging.

In connection with FIG. 11, it should be noted that in connection with tensile strength curves identified as σ_B , the tensile strength of the wire produced in accordance with the present invention before aging has a higher tensile strength than compared to the following of the method of the present invention wherein final aging treatment is employed. In connection with Test IX involving the "H (Hensel Process)," an increase in tensile strength is observed upon an increase in the percent draft. However, it should be noted that the high value in tensile strength is not a necessary requirement for wiring conductors, whereas the properties concerning conductivity, flexibility, releasing force and electrical contact resistance are very important in view of the particular application to which these wires are em-

ployed, that is, wire wrapping termination. It is of sufficient tensile strength if the fine wire made in accordance with the method of the present invention has a tensile strength of 50 kg/mm² or more.

As to elongation as shown in FIG. 11, it can be seen that the method of the present invention before aging has an elongation characteristic approximately equal to the wire product made in accordance with a wire product made in accordance with the prior art. However, as shown in the results of FIG. 11, a remarkable improvement is obtained in elongation after the aging treatment wherein there is shown a value in increased elongation characteristic of 8 percent or more.

In summary, in following the method disclosed by U.S. Pat. No. 2,049,500, the copper alloy having constituents within the ranges disclosed in that Patent could not be readily cold worked to be drawn into a fine wire of less than 1.0 mm without additional heat treatment. After cold working, the flexibility, elongation, releasing force, and conductivity characteristics were found not as good as in wire products by our method, although the tensile strength remained about the same.

In summary, a four-element alloy consisting of 0.2 – 0.5 wt-percent cadmium, 0.05 – 0.2 wt-percent silver, 0.2 – 0.7 wt-percent chromium, and copper which makes up the remainder, is subjected to solution heat treatment for 0.5 – 2 hours at a temperature of 900°C – 1000°C, is then rapidly cooled and is given a combination of cold working which gives a cold draft of 50 percent or more to produce a fine electric wire and a heat treatment of aging treatment for 0.5 – 2.5 hours at a temperature of 450°C – 550°C. It makes it possible to obtain heat-resistant copper alloys for electric conduction suitable for electric wires used for wiring connections which have a great wrapping force and low electric contact resistance.

We claim:

1. A method of manufacturing heat-resistant copper alloy of high ductility to provide for the production of

electrical wire therefrom adaptable for electrical wiring and wire wrapping connections characterized by the steps of providing a four-element alloy consisting of 0.2 – 0.5 wt-percent cadmium, 0.03 – 0.2 wt-percent silver, 0.2 – 0.7 wt-percent chromium and the remainder copper wherein in producing the alloy, chromium, then silver, and then cadmium are added in the named order to the molten copper, subjecting the copper alloy to a solution heat treatment for 0.5 to 2 hours at a temperature of 900°C to 1000°C and thereafter rapidly cooling the alloy, cold working the copper alloy to provide a cold draft of 50 percent or more to draw the same into a fine wire, and thereafter age treating the wire for 0.5 to 2.5 hours at a temperature of 450°C to 550°C.

2. A method of manufacturing heat-resistant copper alloy of high ductility to produce electrical wire adaptable for wire wrapping connections because of improved wrapping force characterized by the steps of first preparing a chromium copper alloy by heating oxygen-free copper in excess of 1000°C and thereafter adding chromium to the molten copper, secondly, adding silver to the molten chromium copper alloy and thirdly, adding cadmium to the molten alloy, all of these constituents added to produce a four-element alloy consisting of 0.2 – 0.5 wt-percent cadmium, 0.03 – 0.2 wt-percent silver, 0.2 – 0.7 wt-percent chromium, and the remainder copper, molding the produced copper alloy ingot, heating and hot rolling the copper alloy ingot at a temperature of 800°C to 980°C, subjecting the copper alloy to a solution heat treatment for 0.5 to 2 hours at a temperature of 900°C to 1000°C, rapidly cooling the copper alloy to maintain at room temperature the solid solution state of chromium in the alloy obtained by solution heat treatment, cold working the copper alloy to provide a cold draft of 50 percent or more to draw the alloy into a fine electrical wire, and thereafter aging by heat treating the wire for 0.5 to 2.5 hours at a temperature of 450°C to 550°C.

* * * * *

45

50

55

60

65