(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 652 943 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.05.2006 Bulletin 2006/18

(21) Application number: **05109964.6**

(22) Date of filing: **25.10.2005**

(51) Int Cl.:
C21D 8/06 (2006.01) *B29D 30/00* (2006.01)
B60C 9/00 (2006.01)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **27.10.2004 US 975811**

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(54) Carburized wire and method for producing the same

(57) A method is taught for processing low carbon steel wire (10) into high carbon steel wire having improved characteristics for use in vehicle tire construction and other applications, including increased wire strength, corrosion resistance and rubber adherence. Low carbon steel wire is carburized to raise carbon content, resulting in increased strength and corrosion resistance. According to other aspects of the invention, the carburization process may occur in the presence of rubber adherence agents (23), which adhere to the steel wire (10), resulting in improved steel rubber adherence in a single processing step.

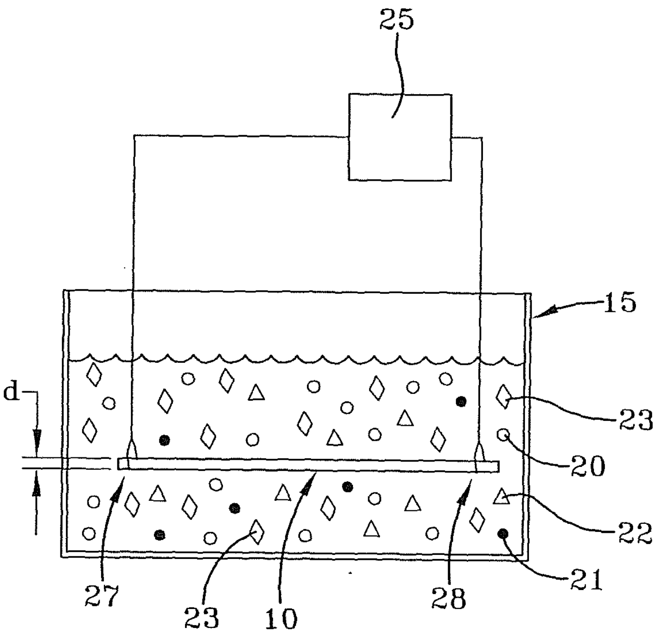

FIG-1

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Description

I. Background of the invention

A. Field of the invention

[0001] This invention relates to a method for carburizing steel and specifically, for increasing the carbon content in low carbon steel wire used in tire construction while improving corrosion resistance and rubber adherence of the steel wire during the carburization process.

B. Description of the related art

[0002] The incorporation of steel belts in vehicle tires has resulted in substantial improvement in tire strength, durability, and performance. Such belts are generally comprised of patterned layers of steel wire embedded into a rubber compound to form a belt. In light of the high stresses found in tires, the physical properties of the wire that is incorporated in the belts, including, the wire's ductility, tensile and impact strength are tightly controlled to produce belts optimized for use in tires. Apart from the physical properties of the steel wire set forth above, other physical characteristics of wire to be used in tires are also important, including corrosion resistance and the ability of the wire to adhere to associated rubber compounds. The adhesion characteristics are especially important to ensure that the wire does not separate from the associated rubber in the belt.

[0003] One component of steel that affects the physical properties of steel wire is the carbon content. Typically, steel wire having high carbon content is used in the construction of belts for tires. High carbon steel has advantageous properties of increased strength, which make it preferable for use in tire applications. By "high carbon steel" is meant steel having a carbon content of between 0.6% and 1.5% carbon content. The adhesion properties of steel wire may be improved by incorporating adhesion improving agents, such as cobalt, copper, or brass, into the wire; however, improving the wire to include these agents currently either involves purchasing more expensive processed wire at the outset or passing the wire through additional processing steps. To avoid additional processing of the wire, tire manufacturers may elect to incorporate adhesion improving agents into the associated rubber rather than into the wire. This method results in improved steel to rubber adherence, but also results in waste of the adhesion improving agents dispersed throughout the rubber, which are not directed solely to the points of contact between the wire and the rubber.

[0004] While high carbon steel is preferable for use in tire applications, it is more expensive to acquire than low carbon steel equivalents. Moreover, steel wire used in the tire industry is often created by drawing the wire to its final diameter. High carbon steel wire is generally relatively more difficult to draw into appropriately sized wire than low carbon steel, resulting in increased manufacturing expenses. Moreover, such wire presently needs to be separately processed in order to add coatings or other agents necessary for improved corrosion resistance and rubber adherence, thereby adding additional processing steps. Tire manufacturers have incurred these additional costs in order to meet the specifications of their tires; however, it would be preferable to produce high carbon, corrosion resistant, rubber adhering steel wire by starting with inexpensive low carbon steel wire and raising the carbon content as well as introducing corrosion resistance and improved rubber adherence in a single processing step. In this way, material costs, processing time and the number of processing steps can be reduced without sacrificing the benefits of high carbon steel wire processed according to existing methods.

[0005] The present invention addresses this problem by proposing a new method for preparing high carbon steel wire for useful applications, by carburizing low carbon steel wire in order to increase the carbon content of the wire and in the same processing period carburizing the wire in the presence of suitable agents for improved corrosion resistance and rubber adherence. In this way, by one process, inexpensive low carbon steel wire can be turned into useful, high carbon, corrosive resistant, rubber adhering wire useful for a variety of applications.

II. Summary of the invention

[0006] According to one aspect of the invention, low carbon steel wire is carburized in the presence of carburizing agents to result in high carbon steel wire.

[0007] According to another aspect of the invention, low carbon steel wire is carburized into high carbon steel with a solid carburizing agent or a liquid carburizing agent or a gaseous carburizing agent.

[0008] According to still another aspect of the invention, low carbon steel wire is carburized in the presence of additives resulting in high carbon steel wire having improved corrosion resistance.

[0009] According to still another aspect of the invention, low carbon steel wire is carburized in the presence of additives resulting in high carbon steel wire having improved rubber adherence.

[0010] According to another aspect of the invention, low carbon steel wire is carburized at a temperature of 1200°C to 1350°C.

[0011] According to still another aspect of the invention, carburized steel wire is rapidly quenched and tempered to produce steel wire useful in construction of vehicle tires.

III. Brief description of the drawings

[0012] The invention may take physical form in certain parts and arrangement of parts, a preferred embodiment of which will be described in detail in this specification and illustrated in the accompanying drawings which form a part hereof and wherein:

FIGURE 1 is a depiction of steel wire prepared for carburization.

FIGURE 2 is a depiction of the cross section of steel wire during the carburization process of the present invention.

FIGURE 3 is an image of the microstructure of a steel wire carburized according to the process taught in the present invention.

FIGURE 4 is another image showing the microstructure of a steel wire carburized according to the process taught in the present invention.

FIGURE 5 is yet another image of a steel wire carburized according to the process taught in the present invention.

FIGURE 6 is a depiction of a carburized steel wire in a quenching medium.

FIGURES 7A-7C are images showing the microstructure of a steel wire carburized according to the process taught in the present invention and specifically Example 1 below.

FIGURES 8A and 8B are images showing the microstructure of a steel wire carburized according to the process taught in the present invention and specifically Example 2 below.

IV. Description of an embodiment of invention

[0013] Referring now to the drawings wherein the showings are for purposes of illustrating a preferred embodiment of the invention. FIGURE 1 depicts a length of steel wire 10 to be carburized in accordance with the processes described herein. In one embodiment, the length of steel wire 10 is a length of low carbon steel wire. By "low carbon steel wire" is meant steel wire having a carbon content of less than 0.25%. It should be noted that steel wire 10 having any carbon content may be used in accordance with the present invention, including, but not limited to steel wire having a carbon content of between 0.25% and 0.5%. Though the increase in carbon content produced in such higher carbon content steel wire by carburization may be proportionately reduced as compared to using low carbon steel wire, other benefits may be induced in such wire by virtue of conducting the carburization process in the presence of corrosion resist agents 22 or rubber adherent agents 23, in accordance with the methods taught herein.

[0014] The steel wire 10 may have a diameter d of between 0.2 millimeters and 2.0 millimeters, though wire of any diameter may be selected with sound engineering judgment. The relatively small diameter d of the steel wire 10 allows for rapid heating and cooling of the steel wire 10, which increases the speed at which the carburization process may take place. The steel wire 10 may be the product of drawing steel stock through a die to reduce the diameter of the steel stock. The steel wire 10 may, however, be formed by any means selected with sound engineering judgment. While the present invention advocates processing steel wire, it should be noted that the present invention may be practiced on other forms of thin steel materials, including, without limitation, steel sheet having a thickness of between 0.2 millimeters and 2.0 millimeters.

[0015] Continuing with reference to FIGURE 1, the steel wire 10 may be placed in a vessel 15. The vessel 15 may be configured to contain a carburizing agent 20 or a carrier medium (not shown) containing a carburizing agent 20. In one embodiment, the carrier medium may be the same as the carburizing agent 20. The dimensions and materials of the vessel 15 may be selected in accordance with sound engineering judgment and may be may be constructed of materials suitable for withstanding the temperatures associated with the carburization process (discussed below).

[0016] It is contemplated that the steel wire 10 may be longer than the vessel 15. In this respect, the vessel may have an inlet and an outlet (not shown) whereby the wire 10 can pass through the inlet, into the vessel 15, and after processing, exit the vessel via the outlet. The steel wire 10 may be provided on a spool located adjacent the inlet. The spool may be rotated so that the wire 10 is substantially continuously fed from the spool, through the inlet, into the vessel 15 where the carburization process occurs, and out the vessel 15 through the outlet. There may be provided a second spool adjacent the outlet for receiving the processed wire 10. Any means for feeding the wire 10 through the vessel 15 may be selected with sound engineering judgment. The feed rate of the wire 10 through the vessel 15 should be sufficiently controlled to allow the carburization process, in accordance with the present invention, to take place. As discussed below, the steel wire 10 may be quenched following the carburization process but prior to being received onto the second spool.

[0017] In the embodiment depicted in FIGURE 1, the carburizing agent 20 may be a liquid carburizing agent. It should be understood, however, that the carburization process of the present invention may occur using liquid carburizing agents, solid carburizing agents or gaseous carburizing agents. Examples of liquid carburizing agents include petroleum-based oils, salt baths, and synthetic mixtures. Examples of solid carburizing agents include carbon black and powdered graphite. Examples of gaseous carburizing agents include methane, propane, ethylene, acetylene and carbon monoxide. Other solid, liquid, and gaseous carburizing agents, which are known in the art and selected with sound engineering judgment, may be used in accordance with the processes disclosed herein. Additionally, as noted above, the carburizing agent 20 may be contained in a carrier medium (not shown), which may be a solid, liquid or gaseous carrier medium.

[0018] In one embodiment, depicted in FIGURE 1, the carburizing agent 20 is a liquid carburizing agent. At least a portion of the steel wire 10 may be immersed in the carburizing agent 20. In one embodiment, the steel wire 10 may be fully immersed in the carburizing agent 20.

The steel wire 10, may be held within the vessel 15 in contact with the carburizing agent 20 by any means selected with sound engineering judgment.

[0019] The vessel 15 may contain other agents in addition to the carburizing agent 20. For example, the vessel 15 may contain more than one carburizing agent 21. Further, the vessel 15 may contain a corrosion resist agent 22. By "corrosion resist agent" is meant materials that are known in the art to improve the corrosion resistance of steel wire. Such materials may include, but are not limited to, materials containing chrome, nickel, vanadium or titanium. The corrosion resist agent 22 may be selected from materials that adhere to the surface of the steel wire 10 or alternatively, from materials that diffuse into the steel wire 10. The corrosion resist agent 22 may be combined with a carrier medium that is the same as the carrier medium, if any, for the carburizing agent 20, or that is a different carrier medium.

[0020] It should be noted that improved corrosion resistance of the steel wire 10 may result from the carburization process, without the addition of a separate corrosion resist agent 22. The carburization process of the present invention may result in the diffusion of carbon from the carburizing agent 20 into the core of the steel wire 10 (shown in FIGURE 2). This infusion carbon into the steel wire 10 may result in a formation of a layer of carbon dense cementite (depicted as 37 in FIGURES 3-5) starting at the surface of the steel wire 10 and extending toward the center of the steel wire 10. The cementite layer 37 resulting from the carburization process may improve the strength of the steel wire 10. The cementite layer 37 also provides a measure of improved corrosion resistance to the steel wire 10 even in the absence of additional corrosion resist agents 22. Accordingly, improved corrosion resistance of steel wire 10 processed according to the present invention may be anticipated without additional corrosion resist agent 22, but may be further improved by carburizing the steel wire 10 in the presence of additional corrosion resist agent 22 as described above.

[0021] The vessel 15 may also contain a rubber adherent agent 23. By "rubber adherent agent" is meant materials that are known in the art to improve the adherence of rubber and rubber-based compounds to steel wire. Such rubber adherent agents 23 may include, but are not limited to materials containing cobalt and copper; however, any such agent selected with sound engineering judgment may be used. The rubber adherent agent 23 may be selected from materials that adhere to the surface of the steel wire 10 or alternatively from materials that diffuse into the steel wire 10. The rubber adherent agent 23 may be combined with a carrier medium that is the same as the carrier medium, if any, for the carburizing agent 20, or that is a different carrier medium.

[0022] While FIGURE 1 shows a vessel 15 containing a carburizing agent 20, corrosion resist agent 22 and rubber adherence agent 23, it should be noted that the invention may be practiced with only a carburizing agent 20 or with a combination of a carburizing agent 20 and one of either a corrosion resist agent 22 or a rubber adherence agent 23.

[0023] Continuing with reference to FIGURE 1, there is provided a heating means 25 operatively coupled to the steel wire 10 for heating the steel wire 10. The heating means 25 may be an induction heating means or a resistance heating means, although any other means for heating the steel wire 10 to a temperature that allows for carburization to occur may be selected with sound engineering judgment. In accordance with the above, the heating means 25 may by an electrical heating means, wherein electricity is conducted to and through the steel wire 10 as a means for heating the steel wire 10. In such an embodiment, there may be provided one or more electrodes 27, 28 which are connected to alternate ends of the steel wire 10. The electrodes 27, 28 may be connected to an electrical source for generating electricity which is passed through the steel wire 10. The heating means 25 may alternatively be an oven or furnace, which may be placed within the vessel 15 or which may be outside the vessel 15. Any heating means 25 capable of heating the steel wire 10 to the appropriate temperature may be selected with sound engineering judgment.

[0024] In one embodiment, the heating means 25 is capable of heating the steel wire 10 to a temperature in excess of 950°C. In an alternate embodiment, the heating means is capable of heating the steel wire 10 to a temperature of between 1200°C and 1350°C.

[0025] Continuing with reference to FIGURE 1, the steel wire 10 in the vessel 15 containing the carburizing agent 20, may be heated by the heating means 25 to a temperature of approximately between 1200°C and 1350°C. As noted above, the vessel 15 may also contain one or more of a corrosion resistant agent 22 and a rubber adherent agent 23. The corrosion resist agent 22 or the rubber adherent agent 23 may be added to the vessel 15 while the steel wire 10 is heated. Alternatively, the corrosion resist agent 22 or the rubber adherent agent 23 may be added to the vessel 15 before the steel wire 10 is heated. In this way, there may be a single processing step for improving the steel wire 10, wherein the corrosion resistance or the rubber adherence or both of the steel wire 10 is improved in the same heating step as is used during carburization.

[0026] As shown in FIGURES 2-5, heating the steel wire 10 in the presence of the carburizing agent 20 may result in carburization of the steel wire 10 as carbon from the carburizing agent 20 diffuses through the surface of the steel wire 10 and into the core of the steel wire 10. Carburization results in an increase in the carbon content of the steel wire 10, which, in turn, may result in the conversion of low carbon steel wire to high carbon steel wire. The relatively high temperatures (between 1200°C - 1350°C) reached during the carburization process may result in an increased rate of carbon diffusion from the carburizing agent into the steel wire 10, which may result in faster processing time from low carbon content to high carbon content. FIGURES 3-5 are images showing a cross-section of steel wire 10 after the carburization process. The cementite layer 37 is the result of the increased carbon content resulting from diffusion of carbon into the wire. As noted above, the cementite layer 37 imparts a measure of corrosion resistance to the steel wire 10 even in the absence of other corrosion resist agents 22. The cementite layer 37 also increases the strength of the steel wire 10, with a deeper cementite layer 37 being related to increased strength. The carburization of the steel wire 10 may be allowed to proceed until the cementite layer 37 is sufficiently present to impart desired strength to the steel wire 10.

[0027] When the carburization process occurs in a vessel 15 containing a corrosion resist agent 22, the corrosion resist agent 22 or elements thereof may either or both affix to the surface of the steel wire 10 or diffuse into the steel wire 10, thereby resulting in improved corrosion resistance (not shown) in the steel wire. In a similar manner, when the carburization process occurs in a vessel 15 containing a rubber adherent agent 23, the rubber adherent agent 23 or elements thereof may either or both affix to the surface of the steel wire 10 or diffuse into the steel wire 10, thereby resulting in improved adherence between the steel wire 10 and rubber compounds as may be used in steel belts for tires. It should be noted that sufficient amounts of carburization agent 20, corrosion resist agent 22 and rubber adherence agent 23 may be added to the vessel 15 to ensure adequate uptake of these elements to sufficiently improve the steel wire 10 to desired levels of strength, corrosion resistance, and rubber adherence.

[0028] As shown in FIGURE 6, at such time as the pertinent properties of the steel wire 10, namely, its carbon content, corrosion resistance, and rubber adherence properties are suitably improved, the steel wire 10 may be quenched in a quenching medium 35. The quenching medium 35 may be any quenching medium that is selected with sound engineering judgment and may include an oil quenching medium or water. One purpose of the quenching medium 35 is to cool the steel wire 10 quickly to a temperature of lower than 200°C and preserve the grain structure of the steel wire 10 after the carburization process.

[0029] The carburization process of the steel wire 10 may result in steel wire 10 having increased carbon content. The carbon content of the steel wire 10 may be increased to a level found in high carbon steel wire (as defined above). In one embodiment, the carbon content of the steel wire 10 may be increased from less than 0.25% to 1.3%. The carbon content of the steel wire 10 may be increased to as high as 4.3% as a result of the processes taught herein. Furthermore, the steel wire 10 may be improved to include improved corrosion resistance and the rubber adherence by means of incorporation of corrosion resist agent 22 or cementite layer 37 and rubber adherence agent 23 on the surface of the steel wire 10 or within the steel wire 23.

[0030] While the cementite layer (shown as 37 in FIGURES 3-5) of the carburized steel wire 10 may cause the steel wire 10 to have increased strength, the cementite layer 37 in the steel wire 10, also may impart an increased brittleness to the steel wire 10. Accordingly, the carburized steel wire 10 may undergo an additional tempering process wherein the steel wire 10 is tempered or annealed to reduce the brittleness created as a result of the carburization process. The tempering process may involve heating and then cooling the steel wire 10 in succession, wherein the steel wire 10 is heated to temperature of between 200°C and 400°C and then cooled to a temperature of lower than 200°C. This tempering cycle of heating and cooling may be repeated. In one embodiment the tempering process may be repeated up to three times. Additional processing steps, including further reduction in the diameter of the steel wire 10 by drawing, may be conducted on the high carbon steel wire produced in accordance with the present invention.

[0031] The various aspects of the invention will be appreciated more fully in light of the following illustrative examples for producing high carbon steel wire in accordance with the present invention.

EXAMPLE 1 - Liquid carburizing

[0032] The carburizing experiment was performed by resistance heating wire in a machine oil. A 6" long pieces of a low carbon wire with 0.2% carbon and diameter of 2 mm was clamped between two electrodes and submerged in a stainless container with dimensions of 12"x4"x4". Heating of the wire was done by using both direct current and alternating current. After heating and cooling the wire inside the oil, it was taken out of the container and cleaned from the oil. Carburized samples were mounted in conductive epoxy mounts, polished, and Nital etched to reveal microstructure of the processed wire. Microstructure of the processed wires was examined in a Leica optical microscope and a Jeol scanning electron microscope. FIGURES 3 and 4 show the obtained microstructure comprised of pearlite and primary cementite. This microstructure is typical for a carbon content close to the eutectic composition of 4.3% carbon. It provides a unique combination of high strength characteristics of cementite and ductility of pearlite. Additionally, a special residue deposited at the surface provided improved steel rubber adhesion.

EXAMPLE 2 - Solid carburizing

[0033] 4" long wires with 0.2% carbon composition and diameters ranging from 0.2 to 1.5 mm were packed with carbon black into a ceramic ladle with a cover. They were heated inside a tube furnace at temperatures ranging from 950°C to 1350°C and times ranging from 5 to 30 minutes. Processed samples were cleaned and metallographic samples were prepared as discussed in Example 1 above. Characterization of the obtained microstructure showed presence of cementite layer in the surface zone of the wire typical for a pro-eutectoid steel with carbon content around 1.3%. Such a cementite layer increases corrosion resistance of steel. Obtained wires were rolled in a wire rolling mill to evaluate wire processability. True strain of up to 2 was achieved without wire breaks. FIGURE 7A shows a transition portion of the rolled wire between the original wire diameter (non-rolled) and a portion with a reduced diameter (rolled portion). FIGURES 7B and 7C show microstructures in the surface layer and in the wire core, respectively. Some of the carburized wires were water quenched and then annealed at 600°C for time ranging from 30 to 120 minutes. As-quenched wires were brittle and cracked during wire rolling (FIGURES 8A and 8B). Annealing resulted in increased wire ductility allowing rolling without cracking. Obtained microstructure of the tempered wires, i.e. quenched and annealed wires, represent a typical spheroidal pearlitic structure in surface layers. In the wire core, microstructure remained predominantly ferritic with some pearlitic colonies typical for low carbon steel.

Claims

1. A method of treating steel wire, the method comprising the steps of:

> providing a length of steel wire (10) having a carbon content at a first carbon level,
> providing at least a first carburizing agent (20),
> providing at least a first rubber adherence agent (23),
> contacting the at least a first carburizing agent (20) and the at least a first rubber adherence agent (23) with the length of steel wire (10),
> providing a heating means (25) for heating the length of steel wire (10),
> operatively coupling the heating means (25) to the length of steel wire (10),
> heating the length of steel wire (10) to a first temperature, wherein the first temperature is between 950°C and 1350°C, and
> heating the length of steel wire (10) at the first temperature until the carbon content of the length of steel wire (10) is at a second carbon level, wherein the second carbon level is higher than the first carbon level.

2. The method of claim 1, wherein the length of steel wire (10) has a diameter of between 0.2 millimeters and 2.0 millimeters, and/or wherein the first carbon level of the length of steel wire (10) is less than 0.5%.

3. The method of claim 1 or 2, wherein the first carbon level of the length of steel wire (10) is less than 0.25%, and wherein the second carbon level of the length of steel wire (10) is greater than 0.6%.

4. The method of at least one of the previous claims, wherein the first temperature is between 1200°C and 1350°C.

5. The method of at least one of the previous claims, wherein the at least a first carburizing agent (20) is selected from the group consisting of solid carburizing agents such as petroleum based oil, liquid carburizing agents and gaseous carburizing agents, and/or wherein the at least a first rubber adherence agent (23) is selected from the group consisting of copper containing rubber adherence agents and cobalt containing rubber adherence agents.

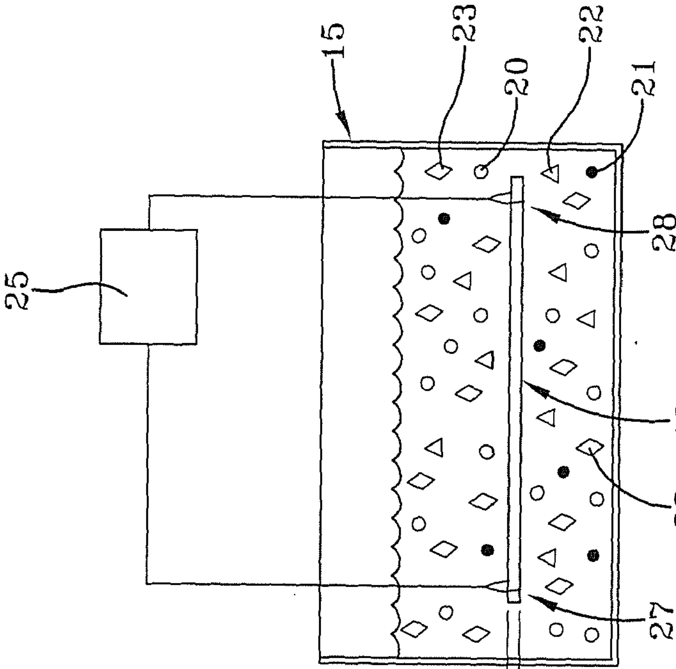
6. The method of at least one of the previous claims, further comprising quenching the length of steel wire (10) to a second temperature, wherein the second temperature is lower than 200°C, and tempering the length of steel wire (10).

7. The method of at least one of the previous claims, further comprising the step of providing at least a first corrosion resist agent (22), and contacting the at least a first corrosion resist agent (22) with the length of steel wire (10) before the step of heating the length of steel wire (10) to a first temperature.

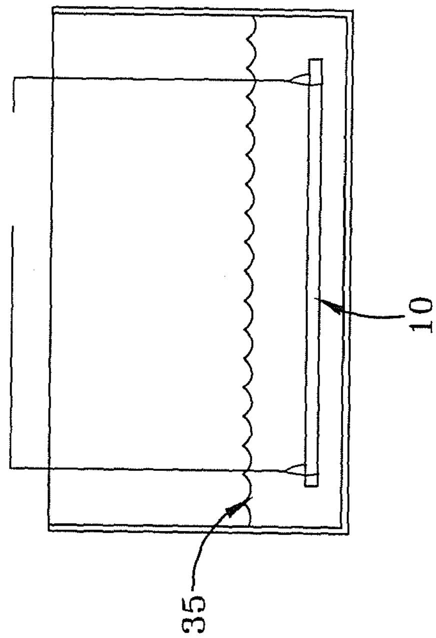
8. The method of claim 1, comprising the steps of:

> providing a length of steel wire (10) having a carbon content at a first carbon level, wherein the first carbon level is less than 0.50%, alternately 0.25%,
> providing at least a first carburizing agent (20),
> providing at least a first rubber adherence agent (23),
> contacting the at least a first carburizing agent (20) and the at least a first rubber adherence agent (23) with the length of steel wire (10),
> providing a heating means (25) for heating the length of steel wire (10),
> operatively coupling the heating means (25) to the length of steel wire (10),
> heating the length of steel wire (10) to a first temperature, wherein the first temperature is between 1200°C and 1350°C,
> heating the length of steel wire (10) at the first temperature until the carbon content of the length of steel wire (10) is at a second carbon level, wherein the second carbon level is greater than 0.6%, alternately 1.0%, quenching the length of steel wire (10) to a second temperate of less than 200°C.

9. Use of the method according to at least one of the previous claims to produce high carbon steel wire for use in vehicle tire construction.



FIG—1



FIG—6

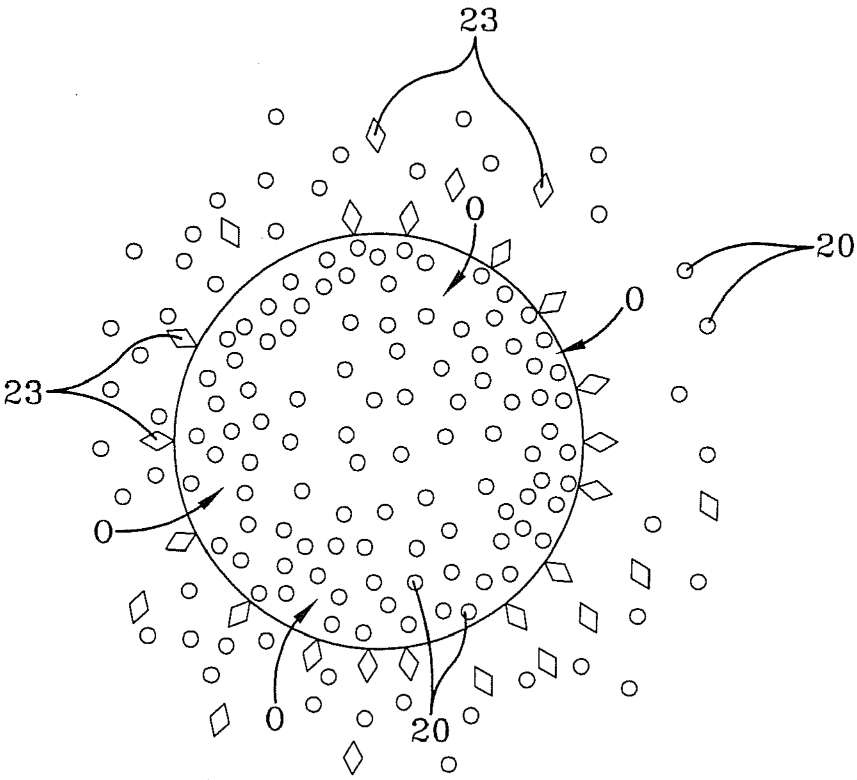


FIG-2

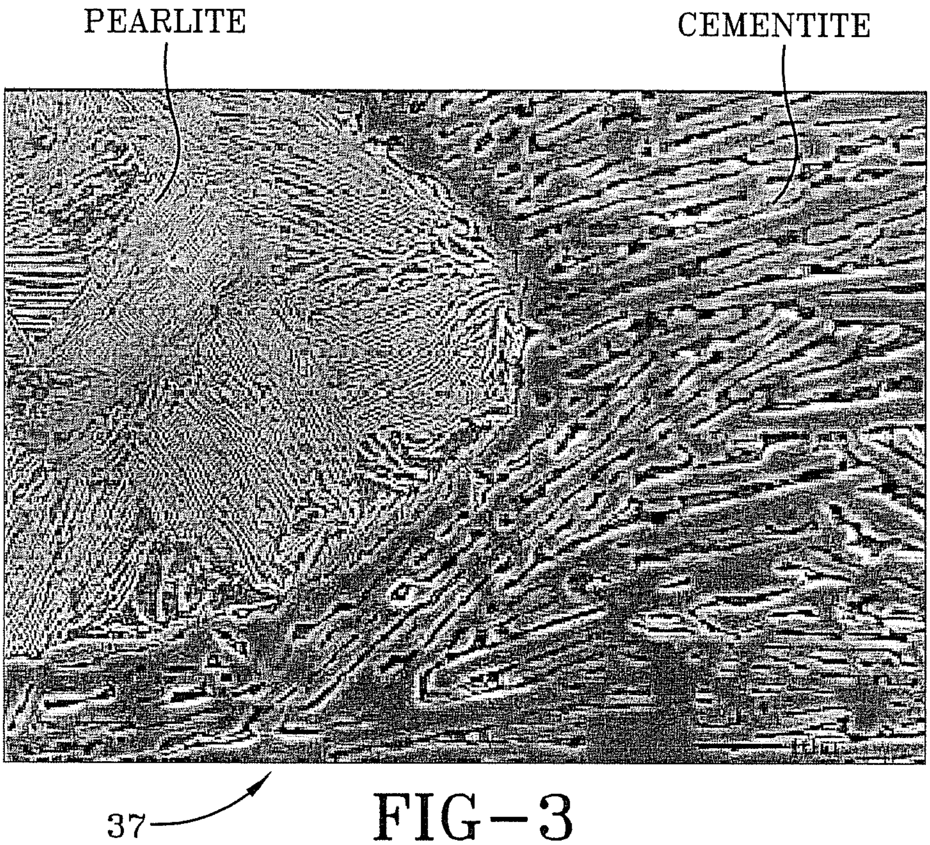


FIG-3

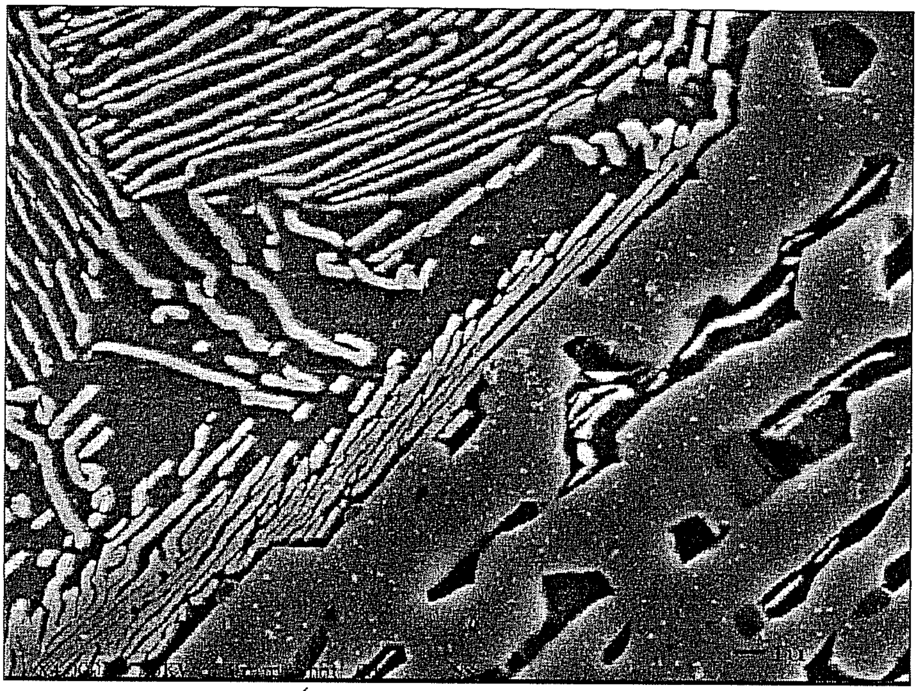


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FIG-4

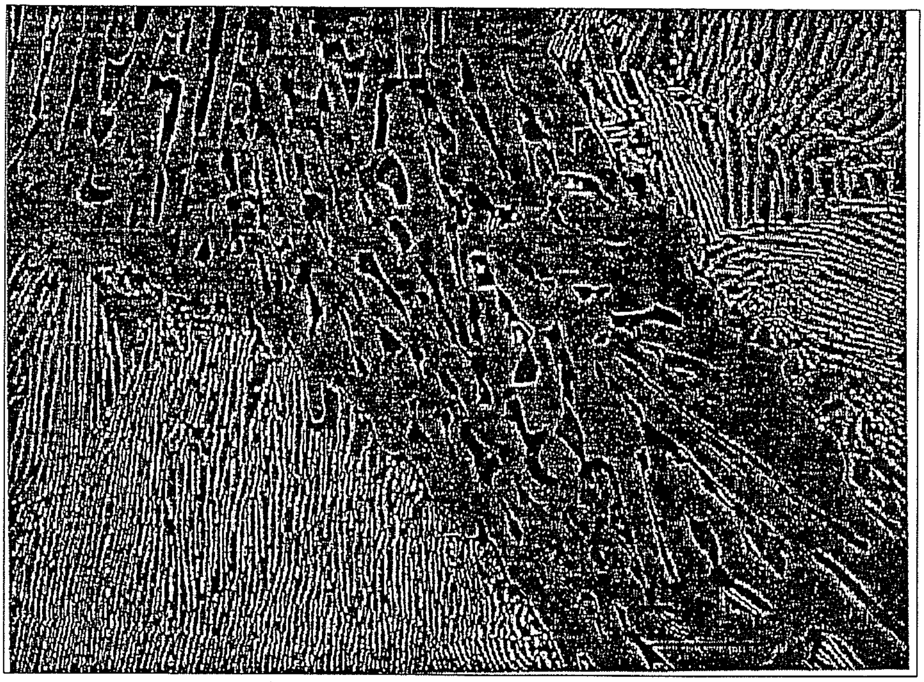

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FIG-5

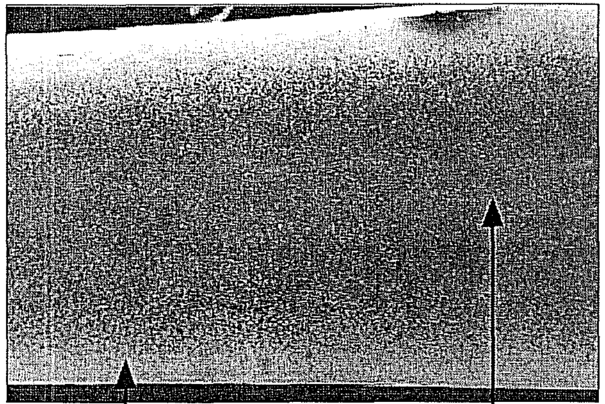
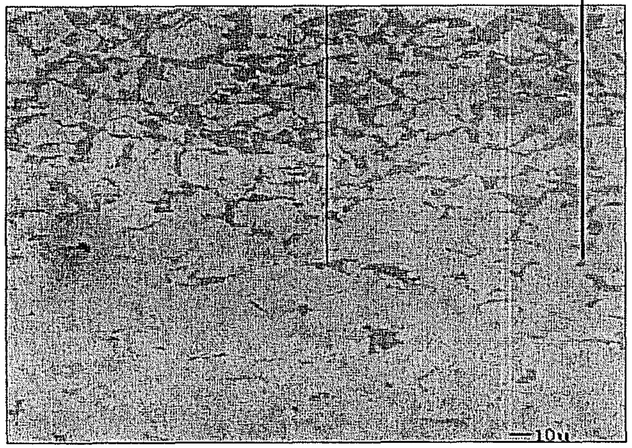


FIG-7A

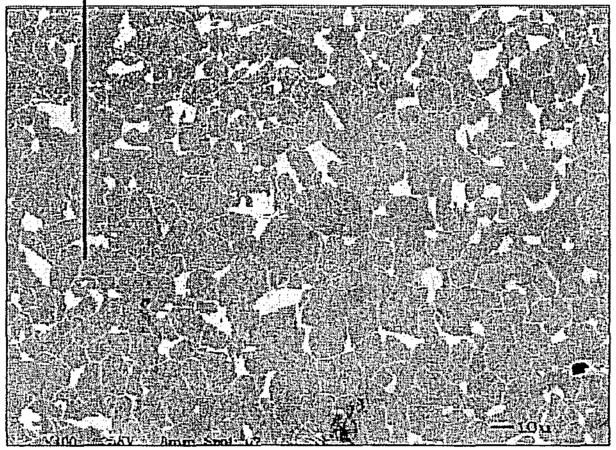
CARBURIZED AND
ROLLED STEEL WIRE



SURFACE

FIG-7B

MICROSTRUCTURE OF CARBURIZED AND
ROLLED STEEL WIRE IN SURFACE ZONE



CORE

FIG-7B

MICROSTRUCTURE OF CARBURIZED
STEEL WIRE IN CENTRAL ZONE

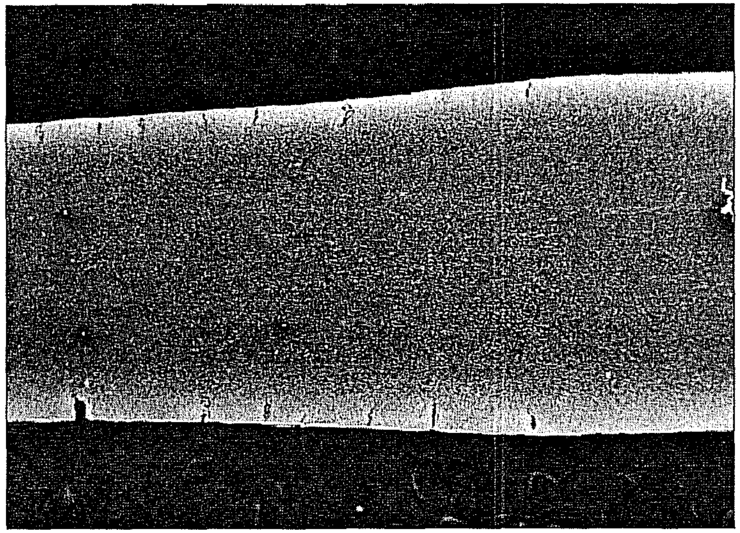


FIG-8A

CARBURIZED, QUENCHED AND AND ROLLED STEEL WIRE

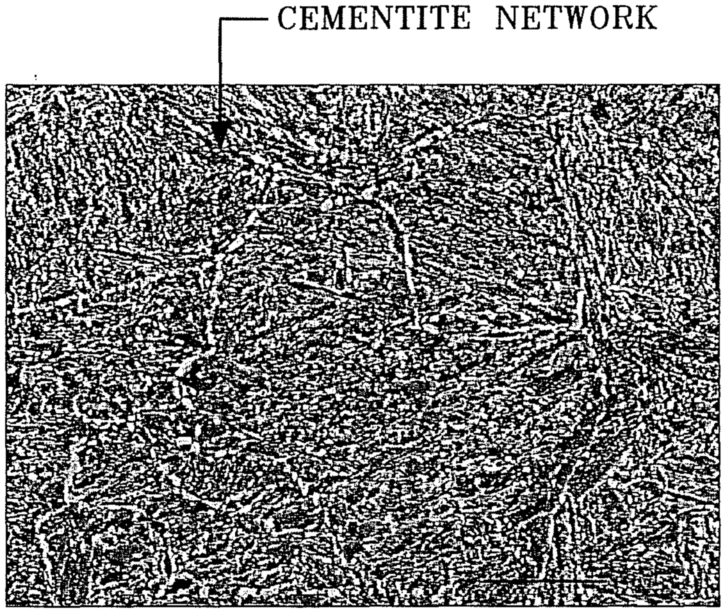


FIG-8B

MICROSTRUCTURE OF CARBURIZED, QUENCHED, ANNEALED, AND ROLLED STEEL WIRE IN THE SURFACE ZONE

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 10 9964

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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