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Oct. 23, 1945.

W. E. LEONARD

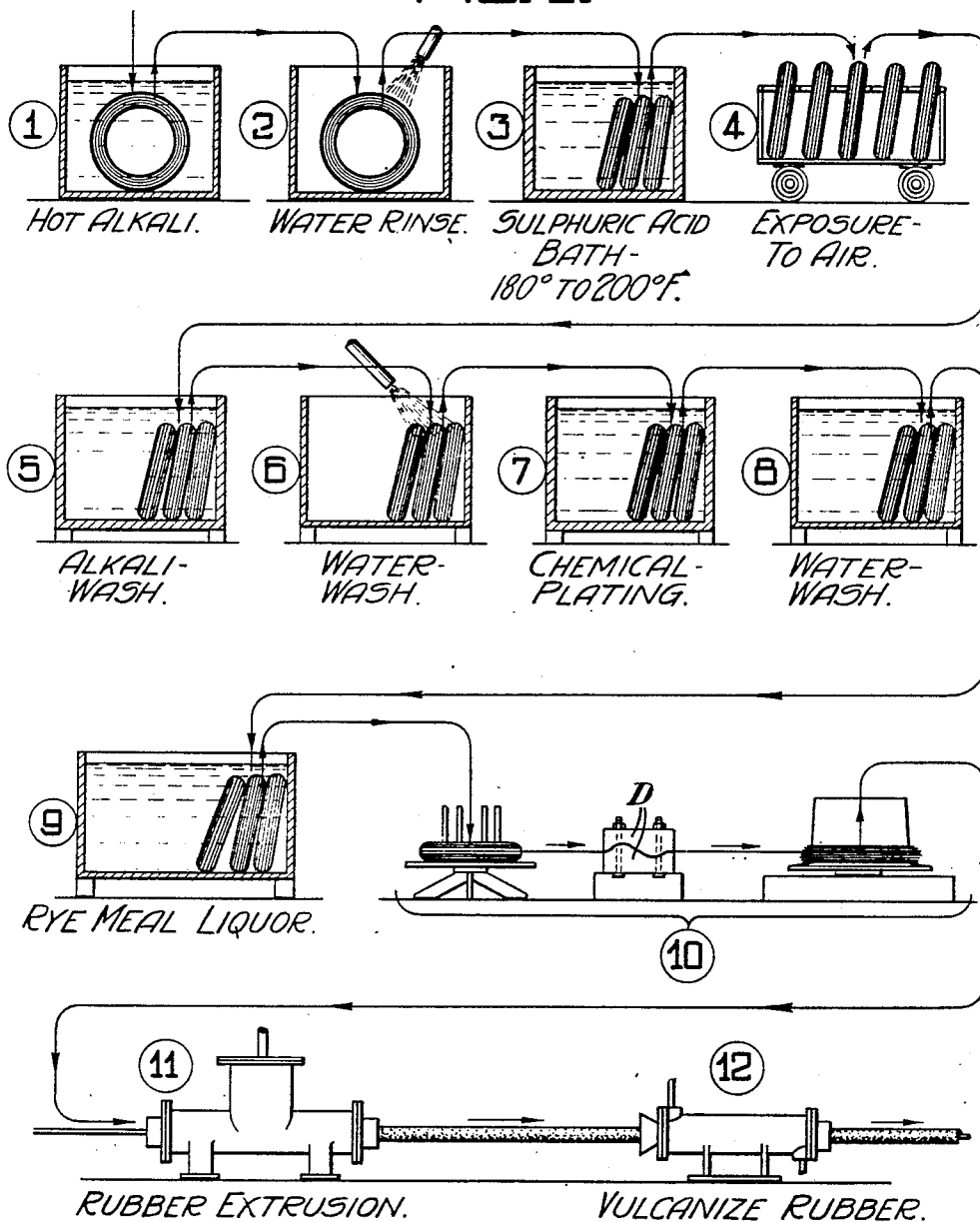
2,387,335

RUBBER ADHERENT WIRE

Filed June 18, 1943

2 Sheets-Sheet 1

FIG. 1.



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83

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2 Sheets-Sheet 2

FIG. 2.

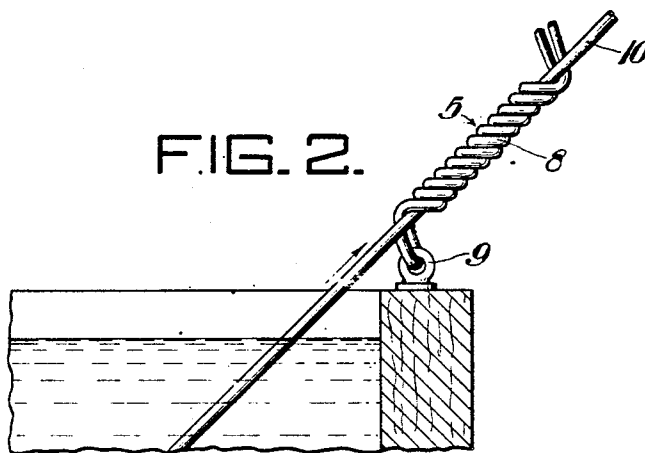


FIG. 3.

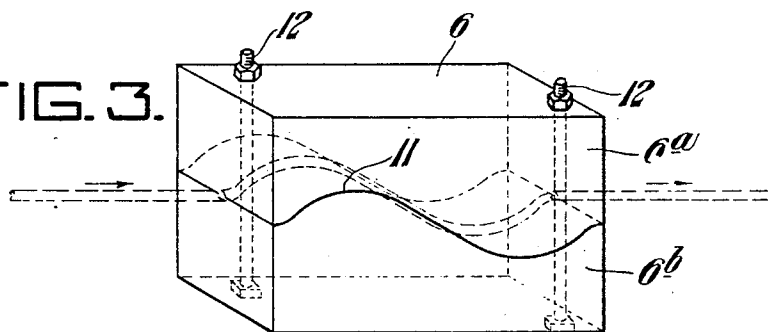
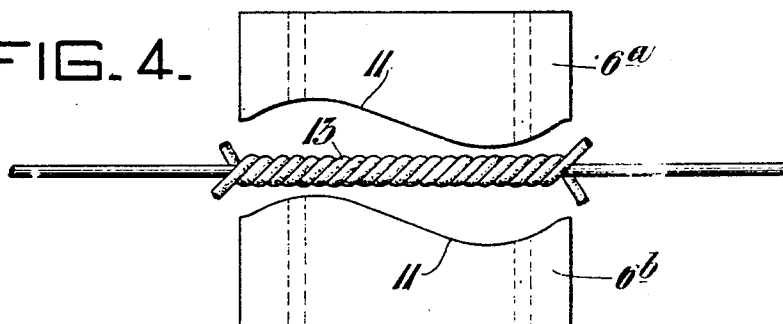


FIG. 4.



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UNITED STATES PATENT OFFICE

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RUBBER ADHERENT WIRE

William E. Leonard, Worcester, Mass., assignor
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New Jersey, a corporation of New Jersey

Application June 18, 1943, Serial No. 491,339

11 Claims. (Cl. 18-59)

The present invention relates to surface treating metal stock, particularly to the surface treating of ferrous metal such as wire, etc., in order to promote those properties of adhesion to rubber, this invention being a continuation-in-part of the invention disclosed and claimed in my copending application Serial No. 351,431, filed August 4, 1940, and entitled "Rubber adherent wire."

The essential steps of the present invention are schematically illustrated in the accompanying drawings, in which:

Figure 1 is a diagrammatic view illustrating the several steps, which are numbered to correspond to the descriptive texts hereinafter set forth in greater detail.

Figure 2 is a detail view of a wipe for round ferrous stock, such as wire, as it emerges from one of the baths of the process.

Figures 3 and 4 are detail views of a special die arrangement through which the elongated metal stock is drawn.

According to the invention, carbon steel wire is bright drawn to finished size in any convenient or conventional manner. The drawn wire is generally accumulated in batches in coiled or bundled form. During the usual wire drawing operation, the surface of the wire becomes covered with a thin film of soap used as a wire drawing lubricant.

The advantageous results of the invention are obtainable by the practice of the following steps:

(1) Each coiled bundle is first given a quick dip in a hot alkali solution whose function is to remove the above mentioned soap film and to thoroughly cleanse the surface of the wire stock prior to the acid etching treatment hereinafter referred to. A suitable alkali solution for this step can be prepared by mixing certain known commercially obtainable ingredients with water. For example, I may prepare suitable alkali solutions by the use of either Oakite No. 24 powder, sold by Oakite Products Incorporated, or Houghton's 127 powder, sold by The Houghton Company of Philadelphia. The composition of said Oakite No. 24 powder is as follows:

	Per cent
Moisture	16.6
Sodium resinate	10.9
Sodium hydroxide	30.8
Sodium carbonate	29.8
Sodium silicate	11.9

The composition of Houghton's No. 127 powder is as follows:

	Per cent
Sodium resinate	14.3
Sodium carbonate	14.9
Sodium hydroxide	28.2
Sodium orthosilicate	23.2
Tri-Sodium phosphate	Trace
Balance inert material including moisture.	

The alkali cleansing solution for step 1 is made by mixing any one or both of the above alkali powders with water, the solution preferably being heated to a temperature of from approximately 180° to 200° F.

(2) After the above alkali cleansing treatment, the coils of wire are washed or rinsed in water, either by dipping in a receptacle or spraying water thereon, as indicated at 2 in the diagram.

(3) As indicated at 3 in Figure 1, the coils of wire are next immersed in a 5% to 6% solution of sulphuric acid, where they are allowed to remain for an interval of about one-half minute. This acid bath is maintained at a temperature of approximately 180° to 200° F. This acid etching step attacks or eats into the surface of the stock by dissolving the iron, and leaves the carbides in the steel in substantially their normal condition, so that as a result of this step 3, a roughened or irregular surface is imparted to the wire stock, but the interior or body of said wire stock is not injuriously affected by the acid.

(4) Thereafter, one or more coils of wire, upon removal from the acid etching bath of step 3, with the acid remaining thereon, are placed on buggies where they are held in the open air and thus subjected to the action of the oxygen in the atmosphere. The time interval for which the wire is subjected to the action of the atmosphere may range anywhere from five minutes to three hours. For example round wire of .006" to .008" diameter will be exposed to the action of the oxygen in the atmosphere for about five minutes, whereas wire of a diameter of approximately .072" may be exposed for approximately three hours. The described quick dip of the coiled wire in the etching bath and subsequent treatment by exposure to atmospheric oxygen is deemed to be highly important, since if the wire were allowed to remain in the acid over an extended period of time, gas due to electrochemical action of acid would make the wire brittle, which is objectionable. In short, it would bring about what is known to those skilled in the art as hydrogen embrittlement.

By giving the wire only a quick dip in sulphuric acid and thereafter holding it for an extended period of time, the roughness obtained by the acid etch is augmented by the action of the adherent acid and the oxygen of the air. In short, the acid dip starts the etching treatment, and the fourth step shown and described results in the obtaining of deeper pits or irregularities in the surface of the wire. This fourth step does not produce that intensive action of acid on the entire mass of the wire such as would be obtained were the wire immersed and held in the acid for a long period of time. The described atmospheric treatment is advantageous, since a satisfactorily roughened or irregular surface is obtained while

83

2

2,387,335

at the same time the wire retains its high tensile strength and ability to resist torsion.

(5) The bundles of etched wire are then given a quick dip, for example, a half-minute immersion, in an alkali solution. A suitable solution for the purpose may be made by dissolving either Oakite No. 24 powder or Houghton's No. 127 powder of the above described compositions, in a body of water.

(6) After the bundles are removed from the alkali bath of step 5, they are then washed or rinsed with plain water, either by dipping in a tank or by spraying as suggested at step 6 in the drawings. The functions of steps 5 and 6 are to remove all traces of acid and to thoroughly cleanse the wire stock in preparation for the subsequent step.

(7) The wire which has been roughened, treated and cleaned according to the steps previously described, is thereafter subjected to a treatment which is effective to apply a metallic layer in such a way that the irregularities of the metal layer will be effectively reflected. This step, as suggested at 7 in the diagram, constitutes immersing the roughened wire in a copper sulphate solution, in the absence of an electric current, to thus chemically deposit a thin film of copper on the roughened ferrous metal base. In practice, it is found that satisfactory results may be secured by the use of either a hot or cold solution. In some cases a tin coating may be applied, but when tin is used the tin sulphate solution must be maintained at a temperature of from 160° to 180° F. In some cases a mixture of copper sulphate and tin will be used, in which case the solution should be kept cold. The wire or other ferrous metal stock is held in either the copper or tin sulphate solutions described for a period of from two to four minutes, depending upon the diameter of the stock under treatment. In treating wire .005 to .020 inch in diameter, it is held in the solution for approximately two minutes. In the treatment of stock of from .037 to .072 inch in diameter, the same is held in the solution for about four minutes.

(8) Following the application of a thin layer by the chemical deposition as set forth in the preceding paragraph, the coils of wire with the thin film of copper or tin or combination of copper and tin thereon, are then washed with cold water, as suggested in step 8 of Figure 1.

(9) Following the water rinse, the coils of wire are placed in a vat or tank containing rye meal liquor, so as to protect the wire from corroding, as indicated at 9 in the drawings.

(10) Following the immersion of the coils in the rye meal liquor referred to, the wire is continuously drawn between dies D, as suggested in step 10 of Figure 1, these dies being so shaped as to provide an undulating pass which is effective to reversely bend the wire and thus effectively work the plated layer on wire and also impart a bright finish thereto, and give the wire the correct cast or set.

(11) After the wire has been subjected to the steps above enumerated, it is fed in a substantially continuous manner through an extrusion apparatus of conventional form suggested at E in Figure 1. The extrusion apparatus is adapted to apply a uniform layer of either natural or synthetic rubber in such a way that the rubber or equivalent layer becomes intimately interlocked with the irregularities of the copper or tin film, which irregularities, it will be remembered, reflect those irregularities effected by the acid

etching treatment, which was augmented by the exposure of the etched wire to the atmosphere. Instead of applying rubber or synthetic rubber, I may apply suitable synthetic resins of known compositions.

Where the term "rubber" is used herein, it is to be understood, therefore, that I may substitute synthetic rubber or suitable synthetic resins as the equivalents of such rubber.

(12) When a rubber layer is applied by extrusion or by any other conventional rubber-applying method, the rubber coating is preferably vulcanized. This is suggested in the step numbered 12 in Figure 1 of the drawings.

After the wire leaves the bath of rye meal liquor suggested in step 9 of Figure 1, it is sometimes desirable to subject it to the action of a wipe 5 such as shown in Figure 2. This wipe consists merely of a length of carbon steel wire 8, doubled on itself and secured in any suitable manner, as by means of an eye 9, the free ends of the wipe being twisted around the wire or rod 10 under treatment. The high carbon strand 8 is coiled or wrapped around the wire stock 10 while the latter is at rest, and is made sufficiently tight so that once the stock 10 is set in motion, the wipe will tend to elongate somewhat under the influence of tension, thus causing the individual convolutions to yieldingly grip the moving stock. This is effective in partially removing the rye meal liquor, and also probably assists in working the copper or other metallic plating into the irregular surfaces of the stock. The working of the stock into the irregularities is made more positive, however, by the reverse bending operation by passage through the undulating pass of the dies D, as suggested in step 10. Satisfactory forms of bending dies are shown in Figures 3 and 4, wherein there is illustrated a split die block made of any suitable material such as shown at 6 in Figure 3. The die block illustrated may be of two half sections of an 8" x 8" timber parted along an undulating plane, as shown at 11, so as to comprise complementary die sections 6^a and 6^b. Suitable clamps or bolts 12 are provided to hold the die sections in proper engagement with the wire during its passage therethrough. During the passage of the wire stock through the undulating pass defined by the die sections 6^a and 6^b, the wire is also subjected to the finishing action of a cotton wipe 13 which is held in place by the clamping action of the die sections. The split die 6 thus simultaneously effects a thorough wiping of the wire, works the plating adhering thereto into the etched irregularities, and imparts to the wire any predetermined set which may be desired to facilitate coiling where a straight wire is not to be produced. The set imparted to the finished product can be varied by varying the shape of the surface of 11 so as to give any desired final form to the wire or rod stock under treatment.

A greatly improved product in the form of wire with an adherent coating thereon results from the practice of the described method. This product, it will be appreciated, is in the form of an elongated rod or wire of ferrous metal, the surface of which has been made irregular by the acid etch and exposure to air. Over the irregular surface there is a chemically deposited film of copper, the film being of substantially uniform thickness, thus reflecting the irregularities in the plated coating. The rubber adheres better to the copper than it would to a ferrous base, and the tenacity of its adherence is augmented by the ir-

regularities referred to. Actual reduction to practice has demonstrated the superiority of the product over copper coated in the ordinary way with a smooth coating.

While in the foregoing disclosure I have recited precise preferred steps which an actual reduction to practice on a commercial scale has shown to be highly desirable, it is not to be construed that I am limited thereto, since various modifications may be made without departure from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. In the treatment of ferrous metal stock to increase its rubber-adherent characteristics, the method which comprises washing the stock in an alkali solution, rinsing the stock in water to remove any adherent alkali, etching the surface of the stock in an acid bath whereby the surface thereof is rendered somewhat irregular, withdrawing the stock from the etching bath and exposing it to the action of atmospheric air for a determined time interval whereby the surface of the stock becomes more deeply etched and irregular due to the combined action of air and acid clinging to the surface, cleaning the stock with an alkali solution and water, chemically depositing a layer of metal over the irregular roughened surface of the thus treated stock whereby the irregularities effected by the prior steps are reflected in the coated stock, and then applying a body of rubber to the irregular chemically deposited metallic layer.

2. In the treatment of ferrous metal stock to increase its rubber-adherent characteristics, the method which comprises washing the stock in an alkali solution, rinsing the stock in water to remove any adherent alkali, etching the surface of the stock in a bath of dilute sulphuric acid whereby the surface thereof is rendered somewhat irregular, withdrawing the stock from the etching bath and exposing it to the action of atmospheric air for a determined time interval whereby the surface of the stock becomes more deeply etched and irregular due to the combined action of air and sulphuric acid clinging to the surface, chemically depositing a layer of metal over the irregular roughened surface whereby the irregularities effected by the prior steps are reflected in the coated stock, cleaning the stock by dipping in an alkali solution and then washing with plain water, and then applying a body of rubber to the irregular chemically deposited metallic layer.

3. In the treatment of ferrous metal wire to increase its rubber-adherent characteristics, the method which comprises washing the wire in a hot alkali solution, applying water to the wire to remove substantially all of the adherent alkali solution, etching the surface of the wire by dipping it in a bath containing approximately five per cent of sulphuric acid maintained at a temperature from approximately 180° to 200° F., said bath being effective to etch the surface of the wire and render it somewhat irregular, withdrawing the thus etched wire from the sulphuric acid bath and exposing it to the action of atmospheric air for an interval of from five minutes to three hours, whereby the surface of the wire becomes more deeply etched and irregular due to the combined action of the air on the acid adhering to the surface, cleaning the stock with an alkali solution and water, chemically depositing, in the absence of electric current, a layer of metal on the etched stock whereby the irregularities ef-

fected by the previous steps are reflected in the coated wire, then applying a layer of rubber to the wire.

4. In the treatment of ferrous metal wire to increase its rubber-adherent characteristics, the method which comprises washing the wire in a hot alkali solution, applying water to the wire to remove substantially all of the adherent alkali solution, etching the surface of the wire by dipping it in a bath containing approximately five per cent of sulphuric acid maintained at a temperature from approximately 180° to 200° F., said bath being effective to etch the surface of the wire and render it somewhat irregular, withdrawing the thus etched wire from the sulphuric acid bath and exposing it to the action of atmospheric air for an interval of from five minutes to three hours, whereby the surface of the wire becomes deeply etched and irregular due to the combined action of the air on the acid adhering to the surface, cleaning the stock with an alkali solution and water, passing the wire through a bath of copper sulphate solution in the absence of an electric current to chemically deposit a film of copper on the surface of the wire whereby the irregularities due to the acid etching will be reflected in the copper film thus applied to thus increase the rubber-adherent characteristics of the wire, reversely bending the coated wire to mechanically work the copper film, and thereafter applying a layer of rubber to the wire.

5. In the treatment of ferrous metal wire to increase its rubber-adherent characteristics, the method which comprises washing the wire in a hot alkali solution, applying water to the wire to remove substantially all of the adherent alkali solution, etching the surface of the wire by dipping it in a bath containing approximately five per cent of sulphuric acid maintained at a temperature from approximately 180° to 200° F., said bath being effective to etch the surface of the wire and render it somewhat irregular, withdrawing the thus etched wire from the sulphuric acid bath and exposing it to the action of atmospheric air for an interval of from five minutes to three hours, whereby the surface of the wire becomes deeply etched and irregular due to the combined action of the air on the acid adhering to the surface, cleaning the stock with an alkali and water solution, passing the wire through a bath of copper sulphate solution in the absence of an electric current to chemically deposit a film of copper on the surface of the wire in such manner that the irregularities due to the etching will be reflected in the copper film thus applied to thus increase the rubber-adherent characteristics of the wire, reversely bending the coated wire to mechanically work the copper film, and thereafter applying a layer of rubber about the thus copper-coated wire and vulcanizing the rubber layer.

6. In the treatment of ferrous metal stock to increase its rubber-adherent characteristics, the method which comprises etching the surface of the stock in an acid bath whereby the surface thereof is rendered somewhat irregular, withdrawing the stock from the etching bath and exposing it to the action of atmospheric air for a determined time interval whereby the surface of the stock becomes more deeply etched and irregular due to the combined action of air and acid clinging to the surface, cleaning the stock with an alkali and water solution, chemically depositing a layer of copper over the irregular roughened surface whereby the irregularities ef-

fecting the prior steps are reflected in the coated stock, and then applying a body of rubber to the irregular chemically deposited metallic layer.

7. A new article of manufacture consisting of a ferrous metal wire characterized by an etched surface, a cuprous plating reflecting the irregularities of the etched surface, and an adherent rubber skin on the plated wire and intimately interlocked therewith by virtue of such irregularities.

8. As a new article of manufacture, a ferrous metal wire characterized by an irregular outer surface, a thin film of copper chemically united to the ferrous metal wire and reflecting the irregularities thereof, and a rubber skin vulcanized thereto and thus interlocked with the irregularities of said copper film.

9. A new article of manufacture consisting of a ferrous metal wire characterized by a deeply etched irregular surface and a cuprous plating

reflecting the deep irregularities of the etched surface, said wire being adapted to have a skin of rubber or synthetic rubber interlocked with the deep irregularities of said cuprous plating.

10. A new article of manufacture, consisting of a ferrous metal wire characterized by a deeply etched irregular surface and a thin film of non-ferrous metal united to the metal wire and reflecting the deep irregularities of the etched surface, said wire being adapted to have a skin of rubber or synthetic rubber adhered to and interlocked with the deep irregularities of said metal film.

11. A new article of manufacture, consisting of a metal wire characterized by a deeply etched irregular outer surface, a thin film of non-ferrous metal united to the wire and reflecting the irregularities thereof, and a rubber skin intimately interlocked therewith by virtue of such irregularities.

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