

Sept. 29, 1942.

E. C. DOMM  
RUBBER ADHERENT METAL

2,296,838

Filed Nov. 1, 1937

*Fig. 1.*

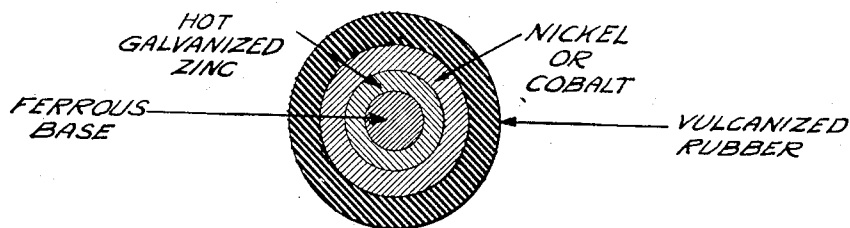
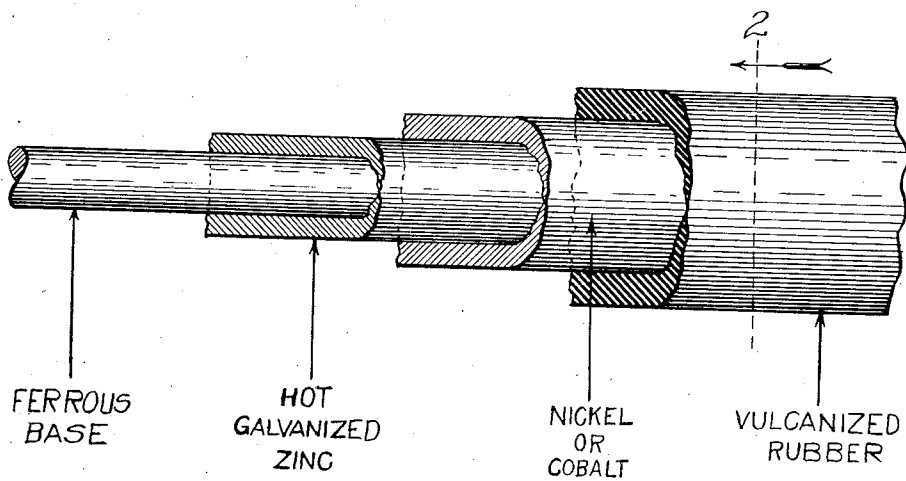


*Fig. 2*

Inventor:  
Elgin Carleton Domm,  
By Christon, Niles, Davies, Kirschley & Dawson,  
Attys

## UNITED STATES PATENT OFFICE

2,296,838

## RUBBER ADHERENT METAL

Elgin Carleton Domm, Niles, Mich., assignor to  
National-Standard Company, a corporation of  
Michigan

Application November 1, 1937, Serial No. 172,305

7 Claims. (Cl. 154—40)

This invention relates to rubber adherent metal, and more particularly to a method of coating ferrous and other metals to make them adherent to rubber. As set forth in my Patent 2,002,261, rubber has been attached to steel by the use of brass coatings produced by dipping or plating in brass, or, as set forth in that patent, by successive coatings with zinc and copper to produce brass upon the article.

It has now been discovered that a coating which is particularly adaptable to various rubber compounds may be produced by combining a nickel coating with an undercoating of zinc. In this operation, cobalt may be substituted for nickel.

An example of the invention will be given in connection with steel tire bead reinforced wires having a diameter of .037 to .043 inch. These wires have a typical composition as follows:

|                                            | Percent |
|--------------------------------------------|---------|
| Carbon .....                               | .65     |
| Manganese .....                            | .80     |
| Phosphorus .....                           | .015    |
| Sulfur .....                               | .025    |
| Silicon .....                              | .095    |
| Balance is iron with traces of impurities. |         |

The wires may be fed continuously from swifts, or the like, through the entire system. They are first cleansed by scraping and then wiping with rags soaked in a grease solvent, such as gasoline. They are then further cleansed by passing through a bath of hydrochloric acid, preferably containing about 10% HCl. The excess acid is removed by wet rags, and the wires then passed through a water bath. They are again passed through acid, this time about 8% HCl and are again wiped and washed. The number and extent of these cleansing treatments depends, of course, upon the original condition of the wire.

The wire, when thoroughly clean, is then hot galvanized in any suitable manner; for example as disclosed in my Patent 2,002,261. In this process the clean wires are drawn through a flux, such as a saturated solution of zinc ammonium chloride, the excess solution is removed by a regular wipe and the wires are then drawn through a bath of molten zinc. The temperature of the bath should be between 820° and 840° F. for steel wire bead reinforcing wires of the composition hereinbefore described. The zinc is deposited to a thickness of approximately  $\frac{1}{40000}$  to  $\frac{1}{11000}$  of an inch. For example, with a wire of .043 inch diameter, weighing 4.88 lbs. per 1000 feet of wire, the weight of

the zinc is about 8 to 20 grams per kilogram of wire. With .037 inch diameter wire, weighing 3.61 lbs. per 1000 feet, the weight of the zinc is about 10 to 24 grams per kilogram.

The zinc alloys itself with the iron to some extent so that about 10 to 25% of the metallic coating is iron. This results in a better bonding than when the zinc is applied electrolytically, but where this bonding action is not required, electrolytic zinc may be used.

After leaving the zinc bath, the excess zinc is removed by an asbestos wiper. The wire may then be cleaned, if desired, and passed to a plating bath.

The nickel or cobalt is applied from any suitable bath of these materials.

The amount of nickel applied should be at least 0.3 gram of nickel per kilogram of wire of tire bead size, and not over 4 grams per kilogram. Preferably a range of .5 to 2.0 grams is employed.

When cobalt is employed, the amount of material should be substantially the same. The preferred amounts correspond to a thickness of approximately  $\frac{1}{60000}$  to  $\frac{1}{240000}$  of an inch. The broader range corresponds about to  $\frac{1}{30000}$  to  $\frac{1}{400000}$  of an inch.

For example, using bead stock A, the following results were obtained:

|                       | Lbs. pull/in. | Percent adhesion |
|-----------------------|---------------|------------------|
| Hot Zn+.5 g. Ni.....  | 83.5          | 82               |
| Hot Zn+1.0 g. Ni..... | 81.0          | 80               |
| Hot Zn+1.5 g. Ni..... | 83.4          | 79               |
| Hot Zn+2.0 g. Ni..... | 83.3          | 92               |

The first column marked "pounds pull over inches" shows the number of pounds pull per linear inch of wire required to pull out a 3-inch wire embedded between two slabs of bead stock and cured and aged between the rubber. The second column shows the percentage of adhesion of rubber to the metal after the break.

Similar wires treated with bead stock B showed the following results:

|                       | Lbs. pull/in. | Percent adhesion |
|-----------------------|---------------|------------------|
| Hot Zn+.5 g. Ni.....  | 86.7          | 65               |
| Hot Zn+1.0 g. Ni..... | 69.6          | 45               |
| Hot Zn+1.5 g. Ni..... | 69.7          | 50               |
| Hot Zn+2.0 g. Ni..... | 67.4          | 45               |

Using cobalt in place of nickel with one particular bead stock showed the following results:

|                       | Lbs. pull/in. | Percent adhesion |
|-----------------------|---------------|------------------|
| Hot Zn+.5 g. Co.....  | 73.4          | 60               |
| Hot Zn+1.0 g. Co..... | 73.6          | 58               |
| Hot Zn+1.5 g. Co..... | 65.6          | 46               |
| Hot Zn+2.0 g. Co..... | 66.3          | 37               |

and another bead stock using cobalt instead of nickel showed the following:

|                       | Lbs. pull/in. | Percent adhesion |
|-----------------------|---------------|------------------|
| Hot Zn+.5 g. Co.....  | 63.8          | 66               |
| Hot Zn+1.0 g. Co..... | 68.8          | 63               |
| Hot Zn+1.5 g. Co..... | 71.8          | 79               |
| Hot Zn+2.0 g. Co..... | 61.2          | 38               |

Salt spray results were considerably better on the whole with cobalt than with nickel.

Tin, cadmium or lead may be substituted for the zinc, particularly with the cobalt, but the results are far less satisfactory, although cadmium and cobalt gave particularly good results with the second bead stock.

An example of the tin and cobalt coating with the second bead stock is as follows:

|                       | Lbs. pull/in. | Percent adhesion |
|-----------------------|---------------|------------------|
| Hot Sn+.5 g. Co.....  | 62.3          | 38               |
| Hot Sn+1.0 g. Co..... | 82.4          | 75               |
| Hot Sn+1.5 g. Co..... | 80.3          | 92               |
| Hot Sn+2.0 g. Co..... | 84.6          | 87               |

The following shows results of cadmium and cobalt on the second bead stock:

|                       | Lbs. pull/in. | Percent adhesion |
|-----------------------|---------------|------------------|
| Hot Cd+.5 g. Co.....  | 74.6          | 64               |
| Hot Cd+1.0 g. Co..... | 83.4          | 97               |
| Hot Cd+1.5 g. Co..... | 89.4          | 97               |
| Hot Cd+2.0 g. Co..... | 83.8          | 100              |

The use of electro-zinc instead of hot zinc gave considerably better results, so far as salt spray results were concerned, but the adhesion was less uniform.

The following table shows the results with the first bead stock with cobalt and nickel:

|                          | Lbs. pull/in. | Percent adhesion |
|--------------------------|---------------|------------------|
| Elect. Zn+.5 g. Ni.....  | 80.0          | 97               |
| Elect. Zn+1.0 g. Ni..... | 76.9          | 93               |
| Elect. Zn+1.5 g. Ni..... | 78.5          | 84               |
| Elect. Zn+2.0 g. Ni..... | 81.1          | 94               |
| Elect. Zn+.5 g. Co.....  | 57.4          | 44               |
| Elect. Zn+1.0 g. Co..... | 54.4          | 34               |
| Elect. Zn+1.5 g. Co..... | 54.0          | 29               |
| Elect. Zn+2.0 g. Co..... | 49.4          | 28               |

When nickel alone is employed with steel wire, the range specified is more critical than when the zinc undercoating or cobalt is used. The results are also much less uniform, but in some cases, it may be desirable to utilize a nickel coating without the undercoating, care being taken as to the selection of the proper bead stock.

The difference in action of different bead stock is well illustrated by the following example of tire bead wire coated with nickel without an un-

dercoating. The first two columns are the first bead stock and the second two columns are the second bead stock:

|               | First bead stock |                  | Second bead stock |                  |
|---------------|------------------|------------------|-------------------|------------------|
|               | Lbs. pull/in.    | Percent adhesion | Lbs. pull/in.     | Percent adhesion |
| .5 g. Ni....  | 44.4             | 6                | 68.0              | 90               |
| 1.0 g. Ni.... | 66.3             | 40               | 67.7              | 18               |
| 1.5 g. Ni.... | 66.3             | 62               | 66.6              | 23               |
| 2.0 g. Ni.... | 64.0             | 57               | 48.6              | 5                |

The invention is illustrated diagrammatically in Figure 1 in which a ferrous wire is shown with a zinc coating, upon which is a nickel or cobalt coating, followed by a rubber coating thereon. Figure 2 is a cross-section along the line 2—2.

While the invention has been illustrated in connection with tire bead wire, it is by no means limited to such articles. In view of the variation in rubber bead compounds, however, the zinc nickel or zinc cobalt combination is of very great advantage where it is known what bead stock will be employed or where it is possible that the formula may be varied from time to time.

The foregoing detailed description has been given for clearness only, and no unnecessary limitations should be understood therefrom.

I claim:

1. An article designed for adherent vulcanization of rubber thereto comprising a metallic base, a metal of the class consisting of zinc, cadmium, lead and tin thereon, and a coating of metal of the class consisting of nickel and cobalt of a thickness of approximately  $\frac{1}{30000}$  to  $\frac{1}{40000}$  of an inch over the intermediate coating.

2. A tire bead wire having a hot galvanized zinc coating thereon and a coating of metal of the class consisting of nickel and cobalt of a thickness of approximately  $\frac{1}{30000}$  to  $\frac{1}{240000}$  of an inch on the zinc.

3. A tire bead comprising a ferrous base tire bead wire, a hot galvanized zinc coating on the wire, a coating of a metal of the class consisting of nickel and cobalt of a thickness of approximately  $\frac{1}{60000}$  to  $\frac{1}{240000}$  of an inch on said zinc coating, said coated wire being vulcanized in a mass of tire bead rubber.

4. The method of preparing a rubber coated object which comprises hot galvanizing a ferrous base, electro-depositing a thin layer of metal of the class consisting of nickel and cobalt upon the galvanized surface and vulcanizing a rubber coating thereon.

5. A rubber coated article comprising a ferrous base, a metal of the class consisting of zinc, cadmium, lead and tin thereon, and a coating of a metal of the class consisting of nickel and cobalt having a thickness of approximately  $\frac{1}{30000}$  to  $\frac{1}{40000}$  of an inch over the intermediate coating.

6. A rubber coated article comprising a ferrous base, a zinc coating thereon, and a coating of a metal of the class consisting of nickel and cobalt having a thickness of approximately  $\frac{1}{30000}$  to  $\frac{1}{40000}$  of an inch over the intermediate coating.

7. The method of preparing a rubber coated object which comprises cleaning a high tensile strength steel wire in dilute hydrochloric acid, removing the acid, applying a hot galvanized coating thereto, electro-depositing a thin layer of nickel thereon, and vulcanizing a rubber coating upon the nickel.

ELGIN CARLETON DOMM.