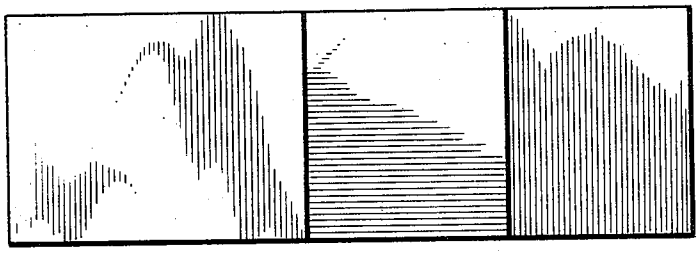
June 8, 1943. M. C. BEEBE 2,320,998

COATING METAL ARTICLES

Filed May 5, 1938

Fig. 1.



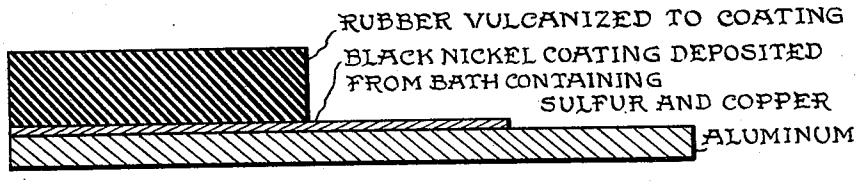



Fig. 2.

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# UNITED STATES PATENT OFFICE

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## COATING METAL ARTICLES

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4 Claims. (Cl. 154—2)

This invention or discovery relates to coating metal articles; and it comprises a method of coating aluminum or other metal articles wherein a suitably cleaned metal surface is provided with a black nickel coating over which rubber is applied by vulcanizing or otherwise, the said black nickel coating then serving as a linking layer bonding rubber to the metal surface; it also comprises improved compositions for and methods of applying the aforesaid black nickel coating; and it further comprises metal articles having rubber bonded thereto through an intervening black nickel coating; all as more fully hereinafter set forth and as claimed.

It is frequently desirable to coat metallic articles wholly or in part with rubber, and in the case of some metals this may be accomplished by vulcanizing the rubber directly onto the metal under suitable conditions of temperature and pressure. Most metals, however, give only a "frictioned" coating of no real adherence.

It is generally difficult to form suitable rubber coatings on aluminum because an aluminum surface does not bond well with rubber. I have found, however, that if the aluminum is provided with a suitable black nickel coating, the rubber may be vulcanized thereon and a durable and satisfactory bond is then produced; the black nickel coating serving as a linking layer. I have further found that this bond is particularly effective if it is formed in the presence of small amounts of copper, which may be either in the aluminous metal itself or in the coating bath from which the black nickel is deposited. The latter condition is advantageous; not only with aluminum and its alloys but with other metals also.

In the accompanying drawing I have shown in exaggerated scale by way of illustration a section of coated article wherein

Figure 1 is a plan view cut away to expose the successive black nickel coating on aluminum and rubber bonded thereto, and

Figure 2 is a vertical sectional view similarly showing the successive laminations.

Coatings of black nickel which are satisfactory for my purposes may be applied to surfaces of aluminous and other metals by electrolytic action or by dipping procedures. A suitable bath for the electrolytic deposition of black nickel is one having the following composition:

| | Oz. per gal. |
|---|---|
| Nickel sulfate | 6 |
| Zinc sulfate | 1 |
| Sodium thiocyanate | 1½ |

The concentrations of the constituents of this bath may be varied considerably, and ammonia or ammonium sulfate may be added if desired. With such a bath, the aluminum article to be coated is connected as the cathode, and nickel anodes are used. Current is applied at a low voltage and low current density; of the order of one or two amperes per square foot, for example. An electrolytic bath of the above composition produces satisfactory coatings on many of the commercial forms of aluminum and its alloys, as well as other metals.

It is often advantageous, and generally less costly, to use a non-electrolytic or dip method of producing the desired black nickel coatings. One bath suitable for dip-coating aluminum or aluminum alloy articles, for example, has the following approximate composition:

| | | |
|---|---|---|
| Water | cubic centimeters | 1000 |
| Ammonium hydroxide | do | 50 |
| Sodium citrate | grams | 50 |
| Nickel acetate | do | 25 |
| Sodium thiosulfate | do | 37.5 |
| Potassium thiocyanate | do | 25 |

A bath of this composition forms a satisfactory black nickel coating with an immersion period of about one minute at a temperature of about 130° F.

The bath compositions described hereinabove are quite satisfactory for use with aluminum alloys and other metals containing amounts of copper up to 5 per cent or more. However, when treating alloys having lower copper contents, and especially those containing less than about 0.5 per cent of copper, it is beneficial to add a small amount of copper salt to these baths. With the above dip-coating bath, for example, I find that about two to five grams of copper acetate per liter may be added, with the desired result of forming a coating giving good adhesion to or bonding with rubber applied thereto. A rubber coating may thus be permanently applied to substantially copper-free aluminum alloys, while black nickel dip-coatings formed on such alloys in baths free from copper salts result in an inferior bond with the rubber.

The addition of copper salt to coating baths is also advantageous in the treatment of copper-containing alloys but to a lesser extent.

Another dip bath embodying my invention has the following approximate composition:

| | | |
|---|---|---|
| Water | cubic centimeters | 1000 |
| Ammonium hydroxide | do | 62.5 |
| Sodium citrate | grams | 25 |
| Nickel acetate | do | 25 |
| Sodium thiosulfate | do | 25 |
| Potassium thiocyanate | do | 25 |
| Copper acetate | do | 2.5 |

This bath deposits a satisfactory black nickel coating on aluminum with only a few seconds immersion, and is effective at moderate temperatures, as low as 90° F.

When the black nickel bonding coat has been produced on the aluminum or other metal surface, either electrolytically or by dipping, as described hereinabove, the rubber coating may be

applied and cured in place by the usual method of vulcanizing with heat and pressure. The black nickel coatings have other utilities in addition to their characteristic of forming sound bonds between rubber and the underlying metal, however, and I consider my coating compositions beneficial and useful, whether or not rubber is applied over the black nickel coatings obtained therewith.

It should be understood that the metal surface must be cleaned and homogenized before the black nickel coating is applied, in order to obtain the best results. Various methods of preparing aluminum surfaces may be employed, but I find that particularly desirable results are obtained if the aluminum is first etched with caustic soda and then immersed in nitric acid. The caustic etching bath may vary considerably in concentration—over a range from 2 per cent to 25 per cent, for example—and the temperature of the bath may also be varied over a range extending up to the boiling point. I find that very satisfactory results are obtained by using a 5 per cent solution of caustic soda at a temperature of 150° to 180° F., with an immersion time of about one or two minutes, depending on the condition of the aluminum surface. It is desirable to then rinse off the caustic as quickly as can conveniently be done, and to follow this by a dip in nitric acid. The concentration of the nitric acid may also be varied, and concentrated acid may be used, or solutions as dilute as 10 per cent. After the nitric acid dip, which need last only a few seconds, the aluminum surface should be washed or rinsed in clean water before it is immersed in the black nickel coating bath.

After the black nickel coating has been applied to the metal surface as previously described, it is customary to clean the surface again if the rubber coating is to be applied thereto. This may conveniently be done in a cyanide bath, which eliminates complex oxides from the metal surface. The rubber composition is then applied with or without a rubber cement, and vulcanized or cured in place at a suitable temperature. A cure for 11 minutes at 316° F. is typical, although the optimum temperature for each particular rubber composition varies somewhat.

Various rubber compositions may be applied over the black nickel coating and, while some work better than others, there seems to be no particular compounding ingredient necessary to obtain a good bond. Typical rubber formulas for this purpose contain 35 to 45 per cent of rubber in the form of smoked sheets or rolled crepe; 45 to 65 per cent of fillers and pigments such as zinc oxide, litharge, magnesia and clay; 1 to 3 per cent of sulfur; and 0.5 to 3 per cent of accelerators, modifiers, etc. When a cement is used, it is conveniently applied in the form of a solution in gasoline prior to the application of the rubber coating itself.

It is to be understood that the specific compositions disclosed hereinabove are mentioned by way of example only, and not by way of limitation, and it is also to be understood that these compositions can be variously modified without departing from the spirit of my invention. For example, in the black nickel dip-coating baths, citric acid and ammonia may be substituted for the sodium citrate specified; and, in general, potassium, sodium and ammonium salts may be used interchangeably.

It appears that satisfactory dip-coating baths are always obtained by adding for each liter of water approximately 40 to 75 cc. of concentrated ammonium hydroxide; approximately 20 to 30 grams of nickel acetate; approximately 20 to 60 grams of alkali citrate; approximately 20 to 30 grams of alkali thiocyanate, and approximately 20 to 50 grams of alkali thiosulfate, with the addition of about 2 to 5 grams of soluble copper salt, such as copper acetate, when desired. Somewhat wider ranges of concentration are also useful.

Other soluble salts which are compatible with the other constituents of the bath may be substituted for the copper acetate and the nickel acetate specified in the above formulas. So far as I am at present advised, however, the acetates are most suitable for this application. The rubber formulas suggested hereinabove may also be modified in ways which are well known in the art.

What I claim is:

1. The method of coating an aluminous metal surface which comprises depositing a black nickel coating thereon by subjecting said surface to the action of a black nickel coating bath containing a dissolved nickel salt, a dissolved sulfur compound and a minor amount of a dissolved copper salt, and thereafter vulcanizing rubber onto the said black nickel coating.

2. The method of coating an aluminum alloy surface containing less than 5 per cent copper comprising applying thereto a black nickel coating by subjecting said surface to the action of an aqueous black nickel coating bath containing a dissolved nickel salt, a dissolved sulfur compound and from 2 to 5 grams of dissolved copper salt per liter, and thereafter vulcanizing rubber onto the said black nickel coating.

3. A method of coating an aluminum alloy surface which comprises depositing a black nickel coating thereon by subjecting said surface to the action of a black nickel coating bath containing in solution a nickel salt, a sulfur compound and a minor amount of a copper salt, and vulcanizing rubber onto the said black nickel coating.

4. An aluminum-surfaced article bearing thereon a coherent black nickel coating characterized by consisting essentially of nickel, sulfur and a minor amount of copper, and a layer of rubber vulcanized to said black nickel coating.

MURRAY C. BEEBE.