Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2306356 A1 2001/10/19

(21) 2 306 356

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) **Date de dépôt/Filing Date**: 2000/04/19

(41) **Mise à la disp. pub./Open to Public Insp.**: 2001/10/19

(51) **Cl.Int.^{7}/Int.Cl.^{7}** F16B 15/00, F16B 33/06

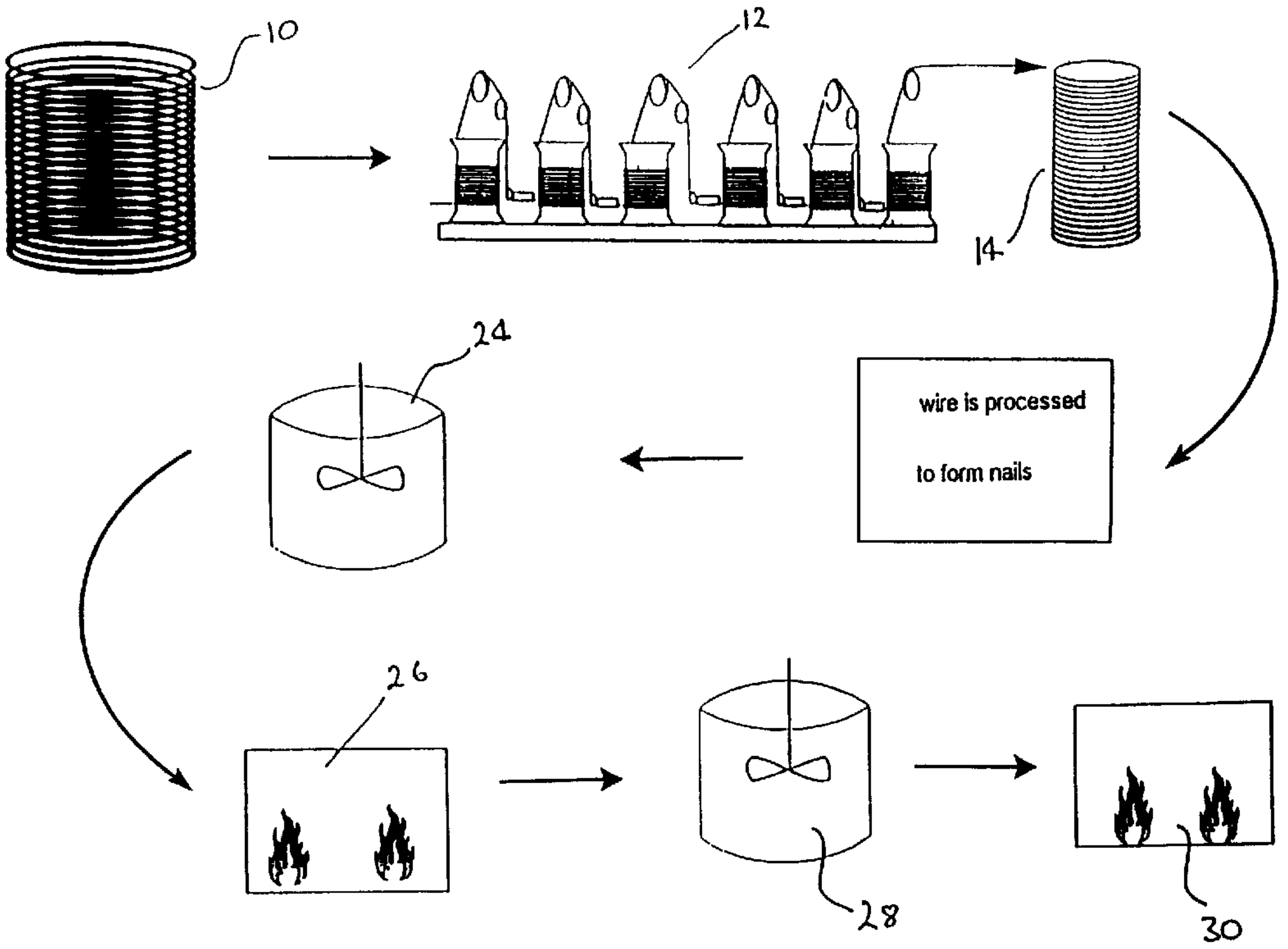
(71) **Demandeur/Applicant:**
BHP STEEL (AWI) PTY LIMITED, AU

(72) **Inventeur/Inventor:**
ZAKRZEWSKI, HENRY, AU

(74) **Agent:** OYEN WIGGS GREEN & MUTALA

(54) **Titre** : UN ORGANE D'ASSEMBLAGE AVEC REVETEMENT PROTECTEUR ET UNE METHODE POUR SA PRODUCTION

(54) **Title:** A FASTENER HAVING A PROTECTIVE COATING AND A METHOD OF PROVIDING SAME



(57) **Abrégé/Abstract:**

There is provided a method of manufacturing a fastener adapted for being driven into a material in use and which has a protective coating for inhibiting corrosion of the fastener. The method comprises forming the fastener from a length of metal and heating the fastener to a desired temperature prior to immersing the heated fastener in a solution containing a passivating agent and one or more polymeric substances. The fastener is subsequently removed from the solution and remaining solution on the fastener is allowed to dry to thereby form the protective coating. There is also provided a fastener manufactured by the method.

ABSTRACT

There is provided a method of manufacturing a fastener adapted for being driven into a material in use and which has a protective coating for inhibiting corrosion of the fastener. The method comprises forming the fastener from a length of metal and heating the fastener to a desired temperature prior to immersing the heated fastener in a solution containing a passivating agent and one or more polymeric substances. The fastener is subsequently removed from the solution and remaining solution on the fastener is allowed to dry to thereby form the protective coating. There is also provided a fastener manufactured by the method.

A FASTENER HAVING A PROTECTIVE COATING AND A METHOD OF PROVIDING SAME

Field Of The Invention

The present invention relates to a metal fastener with a protective coating for inhibiting corrosion of the fastener from occurring as a result of exposure to environmental conditions. There is also disclosed a method for the manufacture of the fastener.

Background Of The Invention

Corrosion of metal fasteners like nails in situ not only shortens their life but may also lead to staining of the material fastened. This can cause unsightly marking of the material and is particularly disadvantageous when the material is relatively permeable to water as metal oxides resulting from the corrosion can spread through the material from the fastener leading to more serious staining than may otherwise occur.

It is known to treat such fasteners with a galvanising or like process to provide them with a protective coating to inhibit corrosion.

In United States Patent No. 5033181 there is disclosed a method of manufacturing nails from pre-galvanized steel rod. The method involves coating the nails once formed from the rod with a polymeric layer to cover exposed steel resulting from loss of regions of the zinc coating during the forming step. This restores corrosion resistance to those regions of the nail on which the zinc was lost and enhances resistance to corrosion over the remainder of the nail where the zinc coating remained in tact. However, the patent offers no solution to how corrosion resistance may be enhanced beyond that provided by the polymeric layer or any means of enhancing adherence of the polymeric layer to the zinc coating or the exposed steel of the nail.

A process for coating a metal fastener with an aliphatic polyurethane resin to protect against corrosion is described in United States Patent No. 5178903. The coating of the fastener is achieved by preferably dipping the fastener into a aqueous dispersion of the resin. Prior to coating the fastener with the resin, the fastener may be galvanised or otherwise precoated with a zinc layer over which a chromate conversion layer is applied. In Japanese Patent Publication No. 62-050480 there is disclosed a steel sheet with a zinc alloy coating and a protective layer of a carboxylated polyolefin resin. The manufacturing process comprises firstly forming a chromate film over the zinc alloy layer and subsequently, coating the chromate film with the carboxylated polyolefin resin. The resulting protective coating again provides enhanced corrosion resistance. However, as two coating steps are involved, such processes are inherently inefficient.

A one-step process for coating a steel sheet is described in Japanese Patent Publication No. 60-190572. In this process, a steel sheet is coated with a composition comprising a mixture of polyethylene resin powder, an aqueous dichromate solution, an organic resin emulsion and a reducing agent prior to the baking the steel sheet in order to form the protective coating thereon. A similar such process is described in Japanese Patent Publication No. 03-215683.

In United States Patent No. 4966634 there is disclosed a process for treating metallic surfaces in order to render them less susceptible to corrosion. The process involves applying an aqueous solution containing an acrylic polymer emulsion and hexavalent chromium ions to the metallic surface enabling chromating and coating of the surface with the before mentioned polymeric material to also be obtained in the one step. That disclosure is directed to the use of polyoxyethylene-polyoxypropylene block polymer in the provision of the acrylic polymer to improve miscibility with chromic acid.

Summary Of The Invention

Broadly stated, the present invention is based on the recognition that heating a metallic fastener prior to coating the fastener with a coating composition containing a passivating agent and a protective polymeric substance may provide the resultant coating when dry with enhanced desirable characteristics.

In one aspect of the present invention there is provided a method of manufacturing a fastener adapted to be driven into a material in use and having a protective coating for inhibiting corrosion of the fastener, wherein the method comprises the steps of:

(a forming the fastener from a length of metal;

(b) heating the fastener to a desired temperature;

(c) immersing the heated said fastener in a solution containing a passivating agent and one or more polymeric substances;

(d) removing the fastener from the solution; and

(e) allowing remaining said solution on the fastener to dry to thereby form the protective coating.

The fastener will generally be a nail, screw, pin, tack or the like and the metal will usually be a ferrous metal. Most usually, the metal will be steel.

Preferably, the fastener will be formed from a length of metal such as coiled metal rod or wire feed, having an existing metallic coating resistant to corrosion. The corrosion resistant metallic coating will typically be a zinc coating and may be formed by a zinc plating, sheradizing, galvanising or other such process.

Although forming the fastener in this manner may result in a sparse covering of the metallic coating in some regions of the fastener such as the head and pointed end of the fastener as may be the case when the fastener is a nail, in these instances there will generally be sufficient such coating on those regions for facilitating adherence of the protective coat formed with further processing of the fastener in accordance with the instant method and for enabling adequate passivation by the passivating agent.

Alternatively, the corrosion resistant metallic coating may be coated on the formed fastener prior to the fastener being heated.

Of the above two options, the former is desirable as processes like galvanising are normally performed at processing facilities distant from where the forming of the fastener occurs, requiring the fasteners to be transported to and returned from such a processing facility before further treatment of the fasteners can proceed. This involves significant time delays. In addition, it is much quicker and more efficient to galvanise, for example, a steel rod and then for the fasteners from the galvanised rod compared to galvanising fasteners in batches. Accordingly, the former option can provide a number of major benefits and more particularly, reduced costs, enhanced ease of handling and far shorter production times.

The term "passivating agent" is to be taken to mean an agent that acts to render the fastener less susceptible to corrosion and includes mixtures of substances. Normally, the passivating agent used in the present method will chemically react and bond with the surface of the metal from which the fastener is formed and/or the corrosion resistant coating on the fastener to thereby reduce the susceptibility of the fastener to corrosion.

Preferably, the passivating agent will form a film of a transition metal over the fastener and be coated by the polymeric substance(s). Most preferably, the passivating agent will be a chromating agent.

The term "polymeric substance" is to be taken to mean a polymer or a mixture of polymers suitable for protecting the fastener against corrosion and capable of fixedly adhering to the passivating agent. Generally, the polymeric substance will consist of one or more synthetic thermoplastic organic polymers. Suitable such polymers include acrylic resins, polyvinylidene resins, vinyl acetate resins and vinyl-acrylic resins including vinylidine-acrylic copolymers. Preferably, the polymeric substance(s) will be selected from the group comprising vinyl-acrylic resins.

Usually, the fastener will be immersed in a solution containing a passivating agent and more than one polymeric substance.

It has been surprising found that heating the fastener prior to immersion in the solution allows excellent coating of the fastener by the solution and enables the subsequent formation of a strongly adherent protective coating with enhanced corrosion resistance to be achieved. Indeed, it is believed that the heating of the fastener is necessary for satisfactory adherence and formation of the coating to occur.

The coating of the fastener by the polymeric substance(s) taken together with the passivation provided by the passivating agent provides significantly greater corrosion resistance compared to that achieved by a metallic corrosion resistant coating on the fastener alone, like that provided by a galvanising or other such process.

Accordingly, the formation of the protective coating on the fastener by the present method may result in a significantly longer working life of the fastener and reduce the risk of the staining of material into which the fastener is driven in use resulting from corrosion of the fastener *in situ*.

Preferably, the fastener is subjected to accellerated drying such as by the application of heat following the removal of the fastener from the solution containing the passivating agent and polymeric substance(s).

In a second aspect there is provided a fastener having a protective coating and manufactured by the inventive method as above described.

Unless the context clearly requires otherwise, throughout the description and the claims, the words ‘comprise’, ‘comprising’, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

The invention will now be further described hereinafter with reference to a number of preferred forms.

Brief Description Of The Accompanying Figure

Figure 1 is a flow diagram illustrating a method for manufacturing a fastener of the invention.

Detailed Description Of Preferred Embodiments Of The Invention

The method illustrated in fig. 1 involves hard drawing a coiled galvanised steel rod 10 having a diameter of about 7 mm using a conventional technique generally indicated by the numeral 12 to form a coil of drawn steel wire 14 having a diameter of about 4 mm. The thickness of the zinc coating on the drawn wire is reduced to about 30μm from a starting thickness on the steel rod of from between about 40μm to about 70μm. Steel rod having a diameter of from between about 5.5 mm to about 9 mm is particularly suitable for use in the instant method. Generally, the diameter of the rod will be drawn down to a diameter of between about 1.85 mm to about 6 mm.

The drawn wire 14 is subsequently formed into individual nails 16 having a shank 18 with a pointed end 20 and a head 22 on the opposite end of the shank. Any known nail forming process whereby the zinc coating substantially remains intact may be used. In the instant study, it has been found that the zinc coating on the pointed end of the nails can remain substantially intact following the formation of the nail and indeed, some zinc remains on the upper surface of the head of the nails although, that covering may be discontinuous.

Rather than using steel wire already having a zinc coating, the nails may be galvanised after they have been formed. This may readily be achieved by immersing the nails into a bath of molten zinc ("hot dipping") or by any other suitable method such as an electrodeposition process.

As indicated in the flow diagram of fig. 1, the nails may be placed in a stirred solvent bath 24 in order to remove any foreign material such as dust, grease, and residual oil or wire drawing lubricant from the surface of the nails. Any suitable solvent that does not significantly affect the zinc coating on the nails may be used. If desired, the nails may be placed in a basket or similar holder to enable placement in and removal of the nails from the solvent bath 24, and to facilitate draining of the solvent from the nails.

Following cleaning of the nails and the removal from the solvent bath 24, they are allowed to substantially dry prior to being placed in a furnace 26 and heated to a temperature in a range of from about 100°C to about 300°C. The temperature to which the nails are heated will vary depending on the diameter of the shank of the nails. Typically, the nails will be heated to a temperature within a range of from about 150°C to about 240°C.

While substantially at this temperature, the heated nails are briefly immersed in a stirred bath of a coating solution indicated by numeral 28, comprising a mixture of between about 15% w/w to about 25% w/w of Novacoat 600 part A [available from Henkel Australia Pty Ltd, Kilsyth, Victoria, Australia] and about 10% w/w to about 25% w/w of Novacoat 600 part B [Henkel Australia Pty Ltd], with water making up the balance of the solution. Usually, the nails will be immersed in the solution for a period of from about 0.1 seconds to about 5 seconds or more. A period of from about 1 to 3 seconds is preferable to ensure complete wetting of the nails. The pH of the coating solution is maintained in a range of from about 1.5 to about 3.3.

The temperature of the solution is maintained in a range of from about 10°C to about 40°C and more preferably, in a range of from about 10°C to about 30°C. It has been found that excessive heating of the solution can cause the solution to gel thereby rendering the solution not suitable for coating purposes.

The nails are subsequently subjected to a blast of dry air at a temperature of from about 120°C to about 125°C in order to dry the nails following their removal from the coating solution. If desired, excess coating solution may be drained from the nails before they are subjected to forced drying. Rather than using hot air to dry the nails, they may alternatively be placed in a drying oven 30 for a predetermined period of time as indicated.

Novacoat 600 part A acts to passivate the nails and so renders the nails less susceptible to corrosion by the formation of a zinc chromate film over the nails. More particularly, it comprises less than about 10% w/w phosphoric acid, less than about 5% w/w chromium trioxide, lithium salt in an amount less than about 10% w/w, zinc phosphate in an amount of about the same as the lithium salt, and about 1% w/w of a surfactant, with the remainder being water.

Novacoat 600 part B in contrast provides an organic polymeric coating for further inhibiting corrosion and more particularly comprises between about 10% w/w to about 60% w/w vinylidine acrylic copolymer latex with the remainder again being water.

Besides acting to passivate exposed surfaces of the nails, Novacoat 600 part A acts as a conversion coating providing a key for promoting adhesion of the polymeric coat provided by the part B solution to the nails.

Accordingly, by immersing the nails in a mixture of both Novacoat solutions significantly enhanced adhesion to the nails of the polymeric substances in the Novacoat 600 part B may be achieved. Although it is preferable to use Novacoat 600 solutions as described above other coating solutions may also be utilised.

The temperature of the nails when immersed in the coating solution is important in ensuring that an adequate and adherent coating forms on the nails. In particular, it is believed that the retained heat in the nails effectively serves as a catalyst in the coating process promoting the rapid evaporation of water, passivation of the zinc coating on the fasteners and cross-linking of the polymeric substances provided by the Novacoat 600 part B solution, resulting in enhanced coating durability and appearance of the formed coating when dry in addition to enhanced corrosion resistance.

It will be appreciated that the coating solution in which the nails are immersed should have a low viscosity to facilitate draining excess solution from the nails and/or drying of the nails and furthermore, to achieve a substantially constant thickness of the resulting protective coating while at the same time avoiding sticking and clumping of the nails together during the drying step.

Advantageously, the resulting coating formed on the nails by the mixture of the Novacoat solutions may enhance the retention of the nails when driven into the timber. It is believed this results from the coat formed from the Novacoat solutions bonding to the timber.

The invention will now further be described with reference to the following Examples.

Example 1

A comparison of the protective effect resulting from the passivation of the zinc coating of galvanised plasterboard nails by immersion in Novacoat part A relative to plasterboard nails not so treated was carried out. All the nails used were formed from hard wire drawn from galvanised steel rod stock and so had an existing protective zinc coating.

The nails were divided into groups of 10 nails each. One test group was immersed in a 25°C stirred bath of 20% w/w solution of Novacoat part A while the second test group was immersed in the same solution but this time at a temperature of 150°C. Following drying of the nails they were subjected to neutral salt spraying (NSS) testing in a cabinet as per Australian Standard AS 2331.3.1-1980. The test was halted once about 5% of the surface of the nails showed red rust. The time for the rust to form was recorded and the results are shown in Table 1.

Table 1: Corrosion Results For Nails Passivated With Novacoat 600 Part A

Sample Tested	Immersion time (mins) in 20% w/w Novacoat 600 Part A	Time to 5% Red Rust (hours)
Plasterboard Nail	0	180
	30 (25°C)	360
	30 (150°C)	340

As can be seen, immersion of the nails in the solution containg Novacoat 600 part A improved the corrosion resistance of the galvanised nails by a factor of about 2 or more relative to a control group not immersed in the solution.

With later studies it was found that the immersion time of the nails could be dramatically reduced while maintaining enhanced corrosion resistance.

Example 2

Samples of 3.75 mm x 75 mm and 2.8 mm x 50 mm bullet head nails formed from hard drawn galvanised steel wire ("drawn nails") were evaluated for corrosion resistance compared to bullet head nails of corresponding size also having a zinc coating that had been formed by sheradising the nails ("plated nails").

Metallurgical investigations showed that the plated nails had a zinc coating mass ranging from about 650 $g.m^{-2}$ for the 50 mm nails up to about 850 $g.m^{-2}$ for the 75 mm nails. The drawn nails were shown to have a zinc coating mass of around 150 $g.m^{-2}$ for the 50 mm nails ranging up to about $250gm^{-2}$ for the 75 mm nails.

Micro-examination of the drawn and plated nails revealed the microstructures of all samples consisted of heavily elongated fine perlite and ferrite. For the drawn samples this is indicative of the drawing of galvanised wire in the formation of those nails while in the plated samples it is indicative of mechanical plating after drawing without any intermediate heat treatment.

The mechanically plated galvanised nails were found to have an average coating thickness on their shank of 100 μm compared to the nails formed by the drawing process which had an average coating thickness on their shank of 30 μm, as determined from transverse sections of the nails.

To evaluate corrosion resistance, nails were placed in a cabinet and subjected to neutral salt spray testing (NSS) as per AS 2331.3.1-1980. For the purpose of evaluation, the nails were completely driven into timber prior to being subjected to the salt spray environment. The end point for testing purposes was taken as being the first appearance of red rust on the heads of the nails. The time taken for the appearance of the red rust was recorded for each group and the results are shown in Table 2.

The corrosion resistance of the above nails following being coated with a mixture of 20% w/w Novacoat part A and 20% w/w Novacoat part B red, blue or green solutions [all available from Henkel Australia Pty Ltd] in water was also evaluated by NSS testing using the same procedure as indicated above. The results are also set out in Table 2.

Table 2: Corrosion Results For Drawn Nails Compared To Plated Nails

Bullet Head Nail	**Hrs to first Red Rust on Nail Head (Test Terminated at 1900 Hrs)**			
	Untreated	Red	Blue	Green
2.8 x 50mm Plated	170	1900	1900	1900
	215	1900	1900	1900
	240	1900	1900	1900
	335		1900	1900
	335		1900	1900
2.8 x 50mm Drawn	240	1010	504	1010
	265	1900	1900	1010
	335	1900	1900	1900
	504	1900	1900	1900
3.75 x 75mm Plated	240	600	335	
	240	1346	670	
	240	1900	1010	
	240	1900	1900	
	240	1900	1900	
3.75 x 75mm Drawn	240	840	432	
	240	1900	672	
	335	1900	1010	
	335	1900	1010	
	380	1900	1900	

Despite the substantially heavier zinc coating mass of the plated nails compared to the drawn nails, and the assumed advantage of the presence of the significant coating of zinc on the head of those nails, the plated nails performed similarly in the NSS test to the drawn nails.

The table further shows that coating the nails with a mixture of both Novacoat 600 part A and part B, substantially increases the corrosion resistance of the nails relative to corresponding groups of nails not so treated. In addition, the table shows that comparable corrosion inhibition results were obtained for the plated and drawn nails coated with the Novacoat mixture.

Example 3

A study was undertaken using plasterboard nails formed from wire hard drawn from galvanised steel wire rod, to determine the effect of applying a mixture of Novacoat 600 parts A and B in inhibiting corrosion of the nails.

Test group 1 comprised plasterboard nails that had been immersed in an solution of 20% w/w Novacoat 600 Part A at ambient temperature for a half hour period. Test group 2 comprised nails preheated to 150°C prior to immersion in a 20% w/w solution of Novacoat 600 part A at ambient temperature, while test groups 3 to 8 comprised nails preheated to 150°C prior to being immersed in a solution of 20% w/w Novacoat 600 part A and 20% w/w Novacoat part B of different colours respectively, namely green, evergreen, orange, red, black and clear [all available from Henkel Australia Pty Ltd].

All test groups in which the nails had been preheated were immersed in the corresponding solutions for the same period of time. The same number of nails were used in each test group. Corrosion was again assessed by neutral salt spray testing

(NSS) as per Australian Standard AS 23313.1-1980. Each group were removed from the salt spray environment when it was estimated that red rust had formed over 5% of the surface area of the nails in the group. The time taken for the formation of the rust was recorded and the results are set out in Table 3.

Table 3: Corrosion Results For Nails With A Coating Formed Form Novacoat 600 Part A And Novacoat 600 Part B

Test Groups	**Hours to 5% Red Rust**
Untreated	180
1	360
2	340
3	2600
4	>2600
5	1200
6	1400
7	2600
8	1200

As can been seen, treatment of the nails with only a 20% w/w solution of the Novacoat 600 part A appears to approximately double the time for corrosion to appear in NSS testing compared to the untreated control group. It is further apparent that when the Novacoat 600 part A and part B solutions were mixed, the protection against corrosion increased by a factor of from about 6.5 when clear part B solution was used up to a factor of 14 or more when the green or evergreen part B solutions were utilised.

Table 3 further shows that significantly greater corrosion protection was afforded to nails preheated to 150°C and treated with both the part A and part B Novacoat 600 solutions relative to nails that were preheated and treated with only Novacoat 600 part A.

Again, later studies have shown that immersion of the nails in both part A and part B Novacoat 600 solutions can be substantially reduced with retention of enhanced corrosion resistance.

Accordingly, although the present invention has been described hereinbefore with reference to preferred embodiments and a number of the examples, the skilled addressee will appreciate that numerous variations and modifications are possible with out departing from the scope of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method of manufacturing a fastener adapted for being driven into a material in use and having a protective coating for inhibiting corrosion of the fastener, wherein the method comprises the steps of:

    (a) forming the fastener from a length of metal;

    (b) heating the fastener to a desired temperature;

    (c) immersing the heated said fastener in a solution containing a passivating agent and one or more polymeric substances;

    (d) removing the fastener from the solution; and

    (e) allowing remaining said solution on the fastener to dry to thereby form the protective coating.

2. A method according to claim 1 wherein the length of metal has an outer corrosion resistant metallic coating of a predetermined thickness and the method further comprises the step of reducing an initial diameter of the length of metal and the thickness of the metallic coating to desired non-zero values prior to step (a).

3. A method according to claim 2 wherein said reducing of the initial diameter of the length of metal and the thickness of the metallic coating is achieved by drawing the length of metal.

4. A method according to claim 2 wherein said reducing of the initial diameter of the length of metal and the thickness of the metallic coating, is achieved by drawing the length of metal.

5. A method according to claim 2 wherein the initial diameter of the length of metal is reduced from a value in a range of from about 5.5 mm to about 9 mm to a value in a range of from about 1.85 mm to about 6 mm.

6. A method according to claim 2 wherein the predetermined thickness of the metallic coating is reduced from a value in a range of from about 40 μm to about 70 μm to a value of about 30 μm.

7. A method according to claim 1 wherein the length of metal has a corrosion resistant metallic coating.

8. A method according to claim 1 further comprising the step of coating the fastener with a corrosion resistant metallic coating prior to step (b).

9. A method according to claim 7 wherein the metallic coating is a zinc coating.

10. A method according to claim 1 wherein the fastener is heated to a temperature of about 100°C or greater prior to immersion of the fastener in the solution.

11. A method according to claim 1 wherein the fastener is heated to a temperature in a range of from about 100°C to about 300°C.

12. A method according to claim 1 wherein the fastener is heated to a temperature in a range of from about 150°C to about 240°C.

13. A method according to claim 1 wherein the passivating agent bonds to the fastener and is coated by the polymeric substance.

14. A method according to claim 7 wherein the passivating agent bonds to the metallic coating and is coated by the polymeric substance.

15. A method according to claim 1 wherein the passivating agent forms a film of a transition metal over the fastener.

16. A method according to claim 7 wherein the passivating agent forms a film of a transition metal over the fastener.

17. A method according to claim 1 wherein the passivating agent is a chromating agent.

18. A method according to claim 17 wherein the chromating agent is chromium trioxide.

19. A method according to claim 1 wherein the polymeric substance is a synthetic thermoplastic organic polymer.

20. A method according to claim 1 wherein the polymeric substance is selected form the group consisting of vinyl-acrylic polymers.

21. A method according to claim 1 wherein the polymeric substance is vinylidine acrylic copolymer latex.

22. A method according to claim 1 wherein the solution contains the one or more polymeric substances in a total amount of from about 1% w/w to about 15% w/w of the solution.

23. A method according to claim 1 wherein the solution further comprises zinc phosphate in a range of from about 1.5% w/w to about 2.5% w/w of the solution.

24. A method according to claim 23 wherein the solution further comprises one or more inorganic acids.

25. A method according to claim 1 wherein the solution has a temperature of about 40°C or less during the immersion of the fastener.

26. A method according to claim 1 wherein the solution is at a temperature in a range of from about 10°C to about 30°C during the immersion of the fastener.

27. A method according to claim 1 wherein the solution has a pH in a range from about 1.5 to about 3.3.

28. A method according to claim 1 wherein the fastener is immersed in the solution for a period of time of up to about 30 minutes.

29. A method according to claim 1 wherein the fastener is immersed in the solution for a period of time of from about 1 second to about 5 seconds.

30. A method according to claim 1 wherein the fastener is formed from a length of steel in step (a).

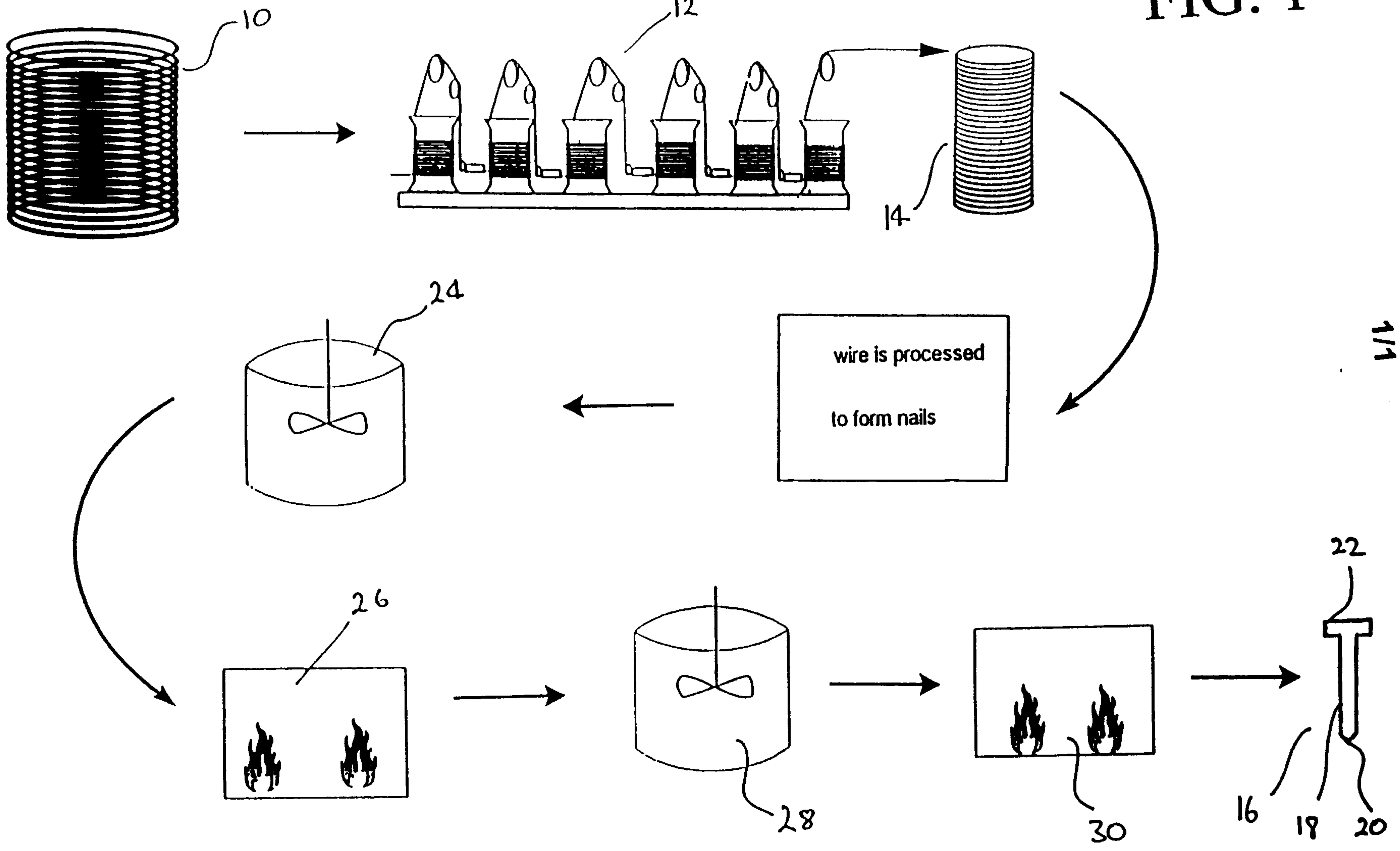
31. A method according to claim 30 wherein the length of steel is coiled steel rod or wire feed.

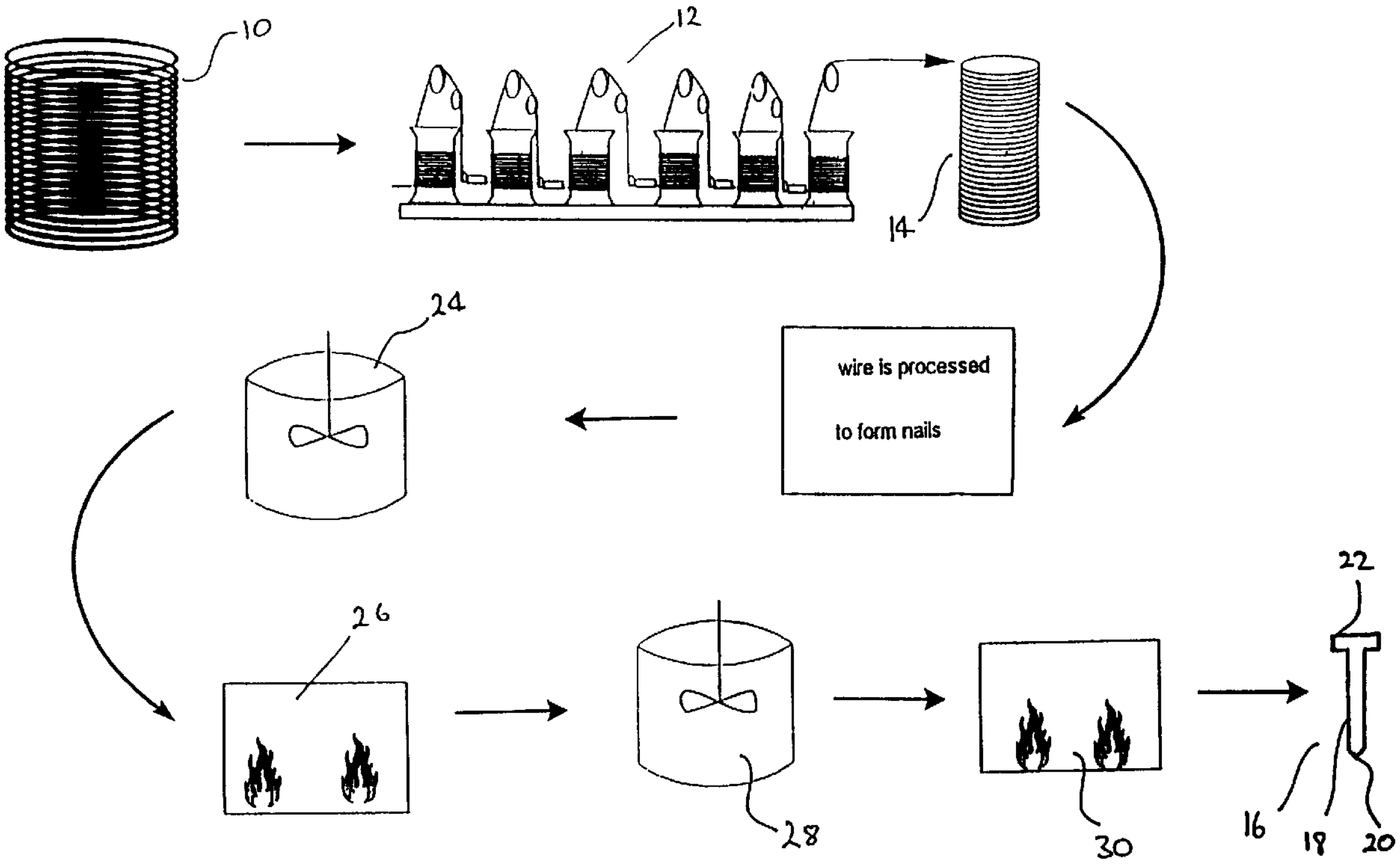
32. A method according to claim 1 wherein the fastener is a screw, tack or nail.

33. A method according to claim 1 wherein the solution in which the fastener is immersed is an aqueous solution.

34. A fastener manufactured by a method as defined in claim 1.

FIG. 1




10
12
14
wire is processed
to form nails
24
26
28
30
22
16
18
20