

Feb. 17, 1970

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METHODS OF SURFACE-TREATING HOOK MEMBERS OF METAL SLIDE
FASTENERS AND SLIDE FASTENERS THUS OBTAINED
Filed June 24, 1966

3,496,004

FIG. 1

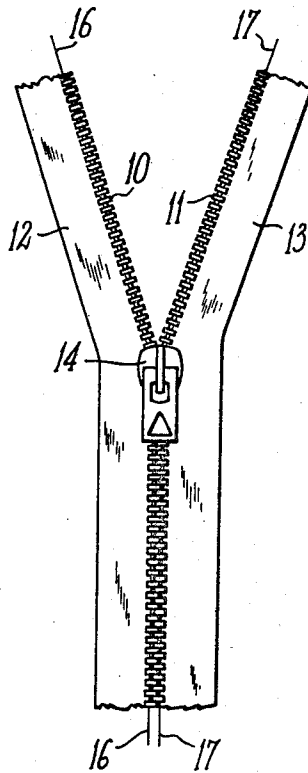


FIG. 2



FIG. 3



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METHODS OF SURFACE-TREATING HOOK MEMBERS OF METAL SLIDE FASTENERS AND SLIDE FASTENERS THUS OBTAINED

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Filed June 24, 1966, Ser. No. 560,207

Claims priority, application France, July 2, 1965, 23,262

Int. Cl. B32b 15/02

U.S. Cl. 117—130

3 Claims

ABSTRACT OF THE DISCLOSURE

A method of coating slide fasteners having hooking elements of copper or alloys of copper, zinc or alloys of zinc, iron or alloys of iron, after mounting upon the textile support and without having recourse to an electric current or to an exterior source of electricity with a coating of tin, cadmium or antimony. The fasteners are immersed with their textile support in a "complex" solution possessing a high electrical potential of tin, cadmium or antimony. The solution has a pH lower than 12 and the temperature is lower than 60° C. and preferably between 30 and 60° C.

This invention is concerned with improvements in the surface treatment of interlocking or hook members of metal slide fasteners.

It is known that most slide fasteners or zippers consist of interlocking members obtained by cutting, stamping or injection from wires, flat sections or like stock of copper alloys (such as tombacs and brasses), aluminum alloys such as "scleral" or "duralinox," or zinc alloys.

According to conventional and old manufacturing methods, these members are barrel-polished and possibly nickel-plated, if stainless slide fasteners are desired, and subsequently set along the edges of textile tapes or ribbons by using so-called "sorting" machines.

It may be noted that nickel-plating (by reduction of nickel ions) and bronzing (by surface oxidation) according to conventional method, as applied to the above-mentioned interlocking members, are still the only surface treatments utilized for copper-alloy or zinc-alloy slide fasteners. More particularly, cadmium plating was never applied owing most probably to its high cost and to the special cares required therefor, and on the other hand the direct chromium plating of these hook members is impracticable in the case of loose small parts. Regarding tinning, this technique was also disregarded due to the readily available advantages and great simplicity characterising the galvanic nickel plating treatment.

At present automatic, high-efficiency machines are increasingly used for simultaneously stamping, cutting and setting the hook members of slide fasteners. Of course, it is no more possible, as contrasted with the hitherto conventional practice, to nickel plate the metal elements of slide fasteners made of copper alloys. Neither could these elements be coated with any protective metallic layer.

Actually, methods of making electrically conducting separate or assembled strips constituting a slide fastener have been developed and carried out in practice, with a view to permit the surface treatment of their component elements by galvanizing, but, save for one exception, it has not been possible to prepare electrolytic solutions preserving the integrity of the dyes and/or fibres of the textile support. The only result thus achieved, under certain specific conditions, was a combined copper and tin coating of copper-alloy slide fastener elements, the combination of these two metals proving to be necessary

for conductivity reasons. Furthermore in this respect, it should be noted that the desired coating does not "catch" on the inner side of the hook portions of the interlocking elements set on the textile ribbons, for galvanic treatments become ineffective or scarcely effective when it is desired to form metal coatings in cavities.

However, slide fasteners, whether they are obtained according to the old method or by applying the new method, consist of hook or interlocking members having a high coefficient of friction, in spite of the polishing operations to which they may be subjected, this coefficient of friction being detrimental to the movements of the sliding element and accelerating the wear thereof, and, therefore, the useful life of the slide fastener. Although nickel plating as applied by the conventional methods of galvanizing to the interlocking members obtained according to the old manufacturing methods will properly protect slide fasteners from oxidation, it cannot overcome the inconvenience set forth hereinabove. The same applies to the above-mentioned combined copper-tin coating method.

Now it was found in the course of many tests having led to the present invention, that a very satisfactory sliding movement of the sliding member could be obtained, even without preliminary polishing the hook members, by coating these members with tin or antimony, or cadmium, or cadmium and tin, or antimony and tin, or vice versa, these three metals actually combining a high resistance to corrosive and oxidizing agents with self-lubricating properties which up to now have neither been evidenced nor utilized.

Under these conditions it is one object of this invention to provide, by way of novel industrial products, slide fasteners wherein the interlocking metal members are "tinned," that is, coated with a more or less thick layer of "tin." The term "tinned" as used herein designates coatings of metals namely tin coatings of antimony, cadmium, as well as antimony and tin coatings, cadmium and tin coatings, and vice-versa, these last named coatings being applied in the form of successive layers.

According to this invention, sliding fasteners can be "tinned" at any desired stage of their manufacture, notably when the interlocking members are completely finished, even when the left-hand and right-hand members of the slide fastener are in their interlocked position. The conditions in which the surface treatment can be applied will be described hereinafter.

This invention, as far as the aforesaid three metals: tin, cadmium and antimony, is concerned, is applicable to all types of sliding fasteners comprising copper or copper-alloy interlocking members, and in the specific case of tin and cadmium, to all types of sliding fasteners having zinc and zinc-alloy interlocking members.

On the other hand it is known that the metals utilized in the manufacture of sliding fasteners are copper alloys, aluminium alloys, zinc alloys, or in the case of "spiral" fasteners, brass wires or stainless-steel wires. It is not apparent, so far, that it has been possible to manufacture commercial-quality sliding fasteners from iron or mild steel stock, in spite of the considerable advantages likely to be derived from the use of these materials, due to the lower cost of ferrous metals in comparison with that of non-ferrous metals.

The present invention, as will be explained presently (and this also constitutes one of its objects), permits of utilizing iron and iron or ferrous alloys in the industry of sliding fasteners by resorting to a suitable coating of tin and/or cadmium and/or antimony, the iron or iron-alloy interlocking members of the sliding fastener which are thus coated and protected having a remarkable resistance to corrosion and oxidation.

In fact, cadmium, like zinc, has electrolytic potential rather remote from that of iron and other ferrous metals, so that it constitutes an efficient anode protection of the metals coated therewith. The same applies to tin and antimony but to a lesser degree.

The present invention therefore includes the "timing" (taken in the meaning given hereinabove) of sliding fasteners made of which the metallic elements consist of metals, namely: copper and copper alloys, zinc and zinc alloys, iron and ferrous alloys, by using coatings of antimony, cadmium and/or tin in single or multiple layers of one of these metals, or successive and/or alternating layers of two or three of said metals.

In this respect it will be noted that the use of suitable metal ion solutions acting without the intervention of electric current, as will be described presently, will coat all the parts of the interlocking members, including the inner faces of the lugs set on the tapes or ribbons, the liquid impregnating these faces by capillarity, the metal ions being deposited without difficulty.

Finally, it will be noted that if antimony is used alone or in admixture with metal salt dyestuffs it permits of obtaining not by surface oxidation but by metal coating the "bronzing" of slide fasteners, notably those intended for military use. Depositing a layer of antimony on tombac interlocking members for "bronzing" or browning same as required for military use increases in very considerable proportions the number of "to-and-fro" movements of the brass sliding member, also required for the same use, which the sliding fastener may withstand before displaying any appreciable wear.

Regarding the practical embodiment of this invention, a distinction should be made between on the one hand the various methods of manufacturing metal sliding fasteners and on the other hand the various solutions likely to be used—whether electrolytic or without using electric current for producing the desired coatings of tin and/or cadmium and/or antimony.

(A) ELECTROLYTIC PROCESSES

(1) In the case of the manufacturing methods set forth in the preamble of this specification, whereby the hook or interlocking members are cut and, after polishing in a barrel or undergoing any other desired mechanical or galvanizing treatments, and possibly after nickel-plating, secured during another operation to textile support tapes, the practical embodiment of this invention is not attended by any particular problem, except for the zinc or zinc alloy elements which must be coppered before tinning them, the tinning, cadmium-plating of ordinary metals, as well as antimony coating, being well known in the art of galvanizing.

Tin, by combining its well known corrosion resistance with a self-lubricating property particularly advantageous as far as the operation of the sliding member along the interlocking members is concerned, will thus constitute an ideal substitute for nickel; if desired, it may be either superposed to the nickel or, finally, combined therewith according to known processes for simultaneously depositing tin and nickel.

However, it should be emphasized that the subsequent steps of setting the interlocking members on the ribbons are likely to develop cracks in the protective coating and therefore lead to small patches, points or incipient rupture lines open to corrosion. Under these conditions it will be specially recommended, according to this invention and in the case of iron or iron-alloy sliding fasteners, to coat the interlocking members with an extremely or relatively thick protective layer so that the latter cannot be deeply affected by the setting operation. An advantageous method of combining this requirement with a bright appearance and a low cost of the sliding fastener, will consist in coating the interlocking members with a suitable layer of zinc or cadmium and to coat this layer in turn with a finishing tin layer to impart a bright appearance to the article.

It will be noted that a fine crystallization of the deposits will reduce the risks of cracking the coating when setting the interlocking members on the textile supports.

(2) In the case of manufacturing methods wherein the interlocking members are simultaneously cut and set on the textile supports, the separate or assembled strips constituting the sliding fastener being unsuitable for conducting current, some means must be provided for ensuring the continuity of the contact between the interlocking members. This feature may be obtained by introducing a conducting wire, for example of aluminium or copper, or a cord or braid surrounded by a coiled aluminium sheath of film, either into the marginal bead of the textile support in which the interlocking members are set, or between the ribbon and the interlocking members when manufacturing the sliding fastener, as practised in the anode oxidation of aluminium or light-alloy sliding fasteners. The continuity of the electric contact between the interlocking members may also be obtained by frictional or sliding contact with a metal conducting wire gauze or with conducting metal rolls, or in any other suitable manner.

The electrolytic baths utilized may be those well known in galvanizing for depositing the metals contemplated in the present invention, but these baths having high concentration of metal salts and being extremely alkaline (tin-cadmium) or very acid (antimony) are obviously noxious to the dyes applied to the textile support and also the strength of the textile fibres incorporated therein, which may even preclude the use of raw or unbleached ribbons. Moreover, the coatings will be deposited with a certain slowness and the elimination of bases and cyanides will require particular care.

Under these conditions, it will be preferable to treat sliding fasteners in the form of separate or assembled strips, especially iron and ferrous-alloy sliding fastenings, according to the non-electrolytic methods to be disclosed presently.

However, in the specific case of tin, a diluted bath that will not be detrimental to the ribbon dye may be used without inconvenience. A typical bath of this character may have the following composition:

Water	-----	liter	1
Tin chloride	-----	gr./liter	10
Trisodic phosphate	-----	do	45
Sodium cyanide	-----	do	10
Temperature	-----	° C	30 to 35
pH	-----		10 to 12

Of course, this is but an example and the proportion of the ingredients as well as the operating temperatures may vary within very wide limits. The trisodic phosphate may be replaced wholly or partly by another alkaline salt capable of hydrolysing, or by a base such as soda or potash, and the sodium cyanide may be replaced by potassium cyanide.

The tin deposit will rapidly attain a thickness of one to two microns.

(B) NON-ELECTROLYTIC, SO-CALLED "IMMERSION" PROCESSES

(1) Chemical displacement process

It is known that if a metal is immersed into a solution of a salt of another metal having a higher rank in the scale of electrolytic values, the surface of the first metal will become under certain conditions coated with a more or less thin layer of the second metal.

However, these solutions operate at relatively high temperatures ranging from 90° to 100° C., and therefore they detrimentally affect the dyes of ribbons or other textile supports. Under these conditions it will be necessary to either operate on raw or unbleached ribbons, or brightening up the dyes after the treatment.

Moreover, although the metal deposits vary rapidly, its

thickness seldom exceeds one-tenth of a micron, since an electrolytic equilibrium develops between the solution and the immersed metal as soon as the latter becomes coated with a metal film containing said solution.

In the case of zinc and zinc alloys, their behaviour is the same as that of copper and its alloys.

Regarding iron and ferrous alloys, these may cause the displacement of antimony ions in very acid solution.

In the present state of our knowledges, and save for the aforementioned exception, depositing cadmium or antimony by chemical displacement is still unknown.

It will therefore be preferable, in most cases, to resort to improved processes of the so-called simple "immersion" type by using solutions of metallic "complexes" for depositing antimony and tin, and to improved processes also of the so-called "immersion" type by using a "contact" metal for depositing cadmium and possibly tin.

(2) Simple immersion process

It is known that "complexes" consist either of the coordination of several radical atoms or molecules about a central metal atom (perfect complex), or of molecular combinations (imperfect complex), which coordination or combination involves an increment in the electric charges of the metal ions and therefore a modification in the electrolytic potential of the "complexed" solution. A typical complex may be for instance the combination of metal salts either with other metal salts or with "neutral" molecules (hydrates ammonia, sodium or potassium chloride, organic amines, cyanides, tartrates, citrates, thiourea, glycocoll, etc.).

According to the present invention "complexes" having the highest possible electrolytic potential will be used.

By way of example, the following complexed solution may be used for depositing pure tin on brass and tombac sliding fasteners:

Water	-----liter--	1
Stannous chloride	-----gr./liter--	2.5
Double sodium and potassium tartrate,		
$C_4H_4O_6NaK$	-----do-----	13
Sodium cyanide	-----do-----	20

Sodium tartrate and potassium tartrate develop with stannous chloride a complex sodium cyanide salt and leads to a solution. By operating at about 35° C., 1 to 2 microns of tins will be deposited within 20 minutes.

This is a "complex" in a state of unstable equilibrium; in other words, the relationship of its component elements does not adhere to the "normal" structural equation. These compounds are particularly active and reactive for being in a state of unstable equilibrium they can easily absorb or lose electrons, thus modifying their oxidation degree or that of the products with which they are put into contact.

The above-specified bath (in a state of unstable equilibrium), even in the advocated diluted form according to this invention, will prove more active for the purpose contemplated than more concentrated solutions but in a state of stable equilibrium.

The following formula exemplifies a typical "complex" in a state of relatively stable equilibrium:

	Gr./liter	
Stannous chloride	-----	2.5
Tartric acid	-----	0.5
Sodium pyrophosphate	-----	15
Sodium cyanide	-----	6
H_2O to make one liter.		

Substantially the same results as with the preceding bath will be obtained, but the lesser cyanide concentration will afford a rapid elimination of this substance from the sliding fastener textile ribbons or like supports by applying a suitable washing operation.

Finally, it will be noted that the addition of thiourea,

for example a few grammes per liter, will accelerate the tin deposit while affording somewhat thicker coatings.

It is also possible to use cyanide-free solutions which are particularly advantageous considering the danger constituted by the handling of this substance and the difficulty of completely eliminating it from the textile supports of the sliding fasteners.

In this case, it is only necessary to "complex" for example tin chloride either with double sodium tartrate and potassium tartrate and thiourea, or with tartaric acid and thiourea.

The best conditions of use of these "complex" tin solutions are a pH value ranging from 8 to 9 and a temperature ranging from 30° to 40° C.

In the case of antimony, various salts of this metal, such as antimony trichloride, antimony trioxide, meta-antimonious acid, etc. will be used by "complexing" them with citric acid, potassium citrate, thiourea, etc.

By way of example, the following formula may be used:

	Gr./liter	
Meta-antimonious acid ($HSbO_2$)	-----	6.5
Sodium hypophosphite (NaH_2PO_2)	-----	5.5
Hydrochloric acid (HCl)	-----	8.5
H_2O to make one liter.		

The optimum conditions of use of "complex" antimony solutions are a pH value ranging from 1 to 3 and a temperature ranging from 50° to 60° C.

(3) Immersion process with a contact metal

It is known that if a metal to be metallized by immersion is caused to contact another, electronegative metal, mostly zinc or aluminium and their alloys in an aqueous solution of metallic ions expected to provide the desired coating, the metallic ions will form on the metal to be coated a layer thicker than those obtained by simple immersion, but these ions are thus also deposited on the contact metal which becomes very rapidly passive and loses its efficiency immediately as a thin metal film builds up thereon.

The thickness of the coatings likely to be thus obtained although greater than that of the coatings obtained by simple immersion, is none the less limited and under the best conditions it cannot exceed a few microns.

According to this invention aluminium and its alloys are used preferably as contact metals and the passivation of the contact metal is avoided by attacking the aluminium or alloy utilized in the process by incorporating soda or potash into the "complexed" solution, either directly or indirectly by hydrolysis of a suitable alkaline salt.

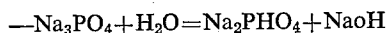
Under the influence of the base, the aluminium will form an aluminate solution with consequent release of hydrogen in the nascent state which activates the reduction of the metal complexes thus dissolved. Moreover, an essential fact to be noted is that the release of hydrogen, through a somewhat mechanical or physical action, prevents the dissolved metallic ions from depositing on the contact surface which thus remains active. Finally, if aluminate ions are released, they will not adhere to the surface to be treated and therefore they will not interfere with the desired deposit or coating.

In practice, the necessary contact may be ensured by one of the processes described hereinabove in Section 1, but it will be advantageous, due to the simplicity of the operation, during the manufacture of the sliding fastener to insert a contact wire between the interlocking members of the sliding fasteners. This wire may consist of a single aluminium or aluminium-alloy filament, or a textile cord of cotton or like material, coated with a thin film of aluminium or aluminium-alloy.

It is worth pointing out that according to this invention and as contrasted with current requirements in the matter of anode oxidation, the contact wire can be broken very frequently, provided that one fragment of the contact wire contacts each member of the sliding fastener, and

the desired effect will be obtained nevertheless. It is even only necessary, when treating the two assembled strips constituting the sliding fastener, that one fragment of the contact wire contacts one of the interlocking members engaging two adjacent members to cause these three members to receive the desired coating.

In the case of tin, the solutions utilized in the simple immersion process may yield thicker coatings, with the contact immersion process, by simply adding a base either directly (soda or potash) or indirectly by hydrolysis of trisodic phosphate or borax, or other alkaline salts. The trisodic phosphate will yield for example soda according to the following reaction:



The minimum amount of soda should be added in order to attack the contact wire without inasmuch damaging the ribbon dye, this amount being of the order of 1 to 2%.

Solutions without cyanide of the type set forth hereinabove may also be used by adding a base thereto.

It is only necessary to "complex," say, tin chloride, with Rochelle salt and/or thiorea, and to add a base as set forth hereinabove.

In the case of cadmium, salts such as cadmium oxide or cadmium sulfate may be used, which will be "complexed" according to the conventional methods of making complexes, as exemplified hereinabove.

The following formula may be used:

	Gr./Liter
Cadmium sulfate $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ -----	7.5
Double sodium and potassium tartrate -----	40
Caustic soda -----	20
Water to make one liter.	

The optimum conditions of use in the cadmium complex solutions are a pH value ranging from 1 to 12 and a temperature ranging from 30° to 40° C.

In the case of antimony, so far as we are aware, the action of a contact metal does not improve the results obtained by the simple immersion process.

The contact immersion process described hereinabove permits of coating iron sliding fasteners treated in the form of separate or assembled strips with cadmium or tin layers of the order of 10 microns ensuring a satisfactory protection against corrosion and oxidation.

(C) FEATURES CHARACTERISING THE IMMERSION PROCESSES, OF THIS INVENTION, WITH OR WITHOUT CONTACT

(1) Of course, the above-described "complexes" correspond to well-defined formulae. However, the proportions of the component elements may be modified without major inconveniences. The component elements in excess will not "complex" but will not inasmuch compromise the action exerted by the solution, provided that they do not precipitate on the contact metal or the surfaces to be treated.

(2) The "complexes" operate under very variable temperature conditions, ranging from room temperature to the boiling point or a temperature approximating this point.

(3) The "complexes" operate under very variable concentration conditions, their dilution attaining up to a few grams per liter of chemicals.

(4) Under the optimum conditions, the "complexes" advocated herein are clear or slightly cloudy, and will not or little affect the dyes or the textile fibres.

(5) The rate of concentration of the base used in the composition of the solutions implemented in the contact processes is quite variable, the lower limit being the attack of the contact metal and the release of hydrogen, the upper limit being the instability of the solution and the turning of the dyes.

It is therefore possible to combine the solution with the temperature and other conditions as a function of the specific conditions of manufacture of the sliding fasteners (i.e. thickness of the desired coating films, rate of

deposit, dye quality, etc.) without departing from the spirit and scope of the invention as set forth in the appended claims.

In the attached drawings, FIGURE 1 illustrates diagrammatically by way of example a sliding fastener of a well-known type comprising metal interlocking members 10 and 11 set on supporting ribbons or tapes 12 and 13, and a sliding member 14. The "contact" metal consists of aluminium wires 16 and 17 threaded between the interlocking members and the ribbons or tapes.

FIGURE 2 illustrates on a larger scale and in cross-sectional view a single hook member 10 coated with a tin layer 18 according to the method of the present invention.

FIGURE 3 illustrates similarly on a larger scale that the contact metal consists of a thin aluminium film 19 coiled around a cotton wick or like cord 20.

What I claim is:

1. A method of coating slide fasteners having hooking elements of copper, zinc, iron or the alloys thereof, mounted upon a textile support without recourse to an electric current or to an exterior source of electricity with a coating of tin, cadmium or antimony comprising immersing said fasteners with their textile support in a "complex" solution having a high electrical potential containing a metal selected from the group consisting of tin, cadmium and antimony, said solution having a pH lower than 12 and the temperature being between 30° and 60° C. and comprising a strong base in a quantity between 1 to 2% of the total volume of said solution, the elements of said slide fasteners being placed in contact with an electronegative metal taken from a group consisting of aluminum, magnesium or their alloys.

2. A method according to claim 1 in which said electronegative metal is aluminum in the form of an aluminum or aluminum alloy wire, wound about a textile wick, said wire being inserted between said hooking elements and said textile support during the fastening thereof.

3. A method of coating slide fasteners having hooking elements of copper, zinc, iron or the alloys thereof, mounted upon a textile support without recourse to an electric current or to an exterior source of electricity with a coating of tin, cadmium or antimony comprising immersing said fasteners with their textile support in a "complex" solution having a high electrical potential containing a metal selected from the group consisting of tin, cadmium and antimony, said solution having a pH lower than 12 and the temperature being between 30° and 60° C., said "complex" solution being carried out in the presence of an electronegative contact metal in a solution such as aluminum, magnesium or their alloys to increase the necessary electric potential by displacing the coating metal, and said contact metal being aluminum in the form of an aluminum or aluminum alloy wire wound about a textile wick inserted between the hooking elements and the textile support during the fastening thereof.

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U.S. Cl. X.R.

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