

UNITED STATES PATENT OFFICE

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ART OF PROTECTIVELY TREATING METALS

No Drawing.

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This invention relates to art of protectively treating metals; and in particular it relates to a process of providing metal or metallized surfaces with a thin coating of a metal resistant to corrosion, wherein the protective metal is employed in a substantially non-aqueous solution, such solution being applied in any suitable manner to the metallic surface to be treated, whereupon the protective metal is deposited in the form of a protective coating or skin. The invention also comprises novel compositions of matter useful in employing and carrying out the process, and also novel products resulting from the process.

For the protection of structures and articles made of iron or steel, for example, against corrosion due to atmospheric and other influences, numerous methods of treatment have been proposed heretofore in the art and some of these have gone into practical use with some degree of success. In particular, it has been proposed to provide the surface to be protected with a metal or alloy coating or skin which is either more resistant to corrosion than the underlying metal or is preferentially attacked by the corroding agencies involved. Thus, galvanizing, sherardizing, and tinning are methods widely used for this purpose. In some special arts, as in the manufacture of gun barrels for example, protective coatings of other metals, including antimony, have been employed. The covering of iron and steel surfaces with a coating of lead has also been practiced to some extent.

The foregoing prior methods of protecting metal surfaces all involve special methods of treatment which are more or less difficult and complicated. Usually it is essential to carry out the treating process with the aid of heat at relatively high temperatures, while in some instances electroplating from aqueous baths of special composition under carefully regulated conditions has been resorted to.

The present applicant has discovered that by proceeding in accordance with the principles of the invention hereinafter to be more fully explained, excellent protection of corrodible metallic surfaces may be attained in a relatively simple manner and in many cases at lower cost than has been possible hereto-

fore, a superior degree of protection being afforded and certain additional advantages being realized.

In general, the process of the present invention comprises subjecting the surface of metal to be protected to the action of a non-aqueous solution of a compound of another metal which is more resistant to corrosion than the first mentioned metal in such manner that such more resistant metal is deposited from its solution upon the first metal. Usually the protective metal used is electronegative with respect to the metal upon which it is to be deposited. More specifically, the novel process comprises subjecting iron or steel surfaces to the action at ordinary temperatures of a solution of a non-ferrous metal compound, especially a heat stable salt of an antimony group metal such as antimony itself, in a non-aqueous solvent, which is fluid at atmospheric pressure and temperature and which is capable of dissolving the metal compound in sufficient quantity and also capable of releasing the protective metal without the aid of an electric current, when the solution is brought into contact with the metal surface to be protected, in such manner that an adequate film or like coating of the non-ferrous metal is formed on the iron or steel. The iron or steel may have been previously provided with a coating of another metal more electropositive than said non-ferrous metal, as by galvanizing, sherardizing, or other metallizing process; in which case the protective coating of the present novel process may be superposed upon such previously applied metal coating.

Without intending thereby to limit the scope of the invention, reference will be made hereinafter more particularly to the employment of antimony compounds in accordance with the principles of the invention, it being understood that this is merely for the purposes of explaining and illustrating the underlying principles here involved. With this same purpose in view, certain specific non-aqueous liquid solvents will be mentioned hereinafter, but it is to be understood that these are merely typical of non-aqueous sol-

vents that may be employed in practicing the invention.

In a specific example embodying the principles of the invention, it will be assumed that sheet iron is to be treated in accordance with the process of the invention. The term iron is used in the present specification and claims to include not only iron strictly speaking but also steel in its various forms. It has been found that the invention can be practiced to greatest advantage if the sheet iron has already received a coating of a metal, such as zinc, that is more electropositive than iron. Therefore, if the iron has not already received such a coating, this may advantageously be applied by a suitable galvanizing or sherardizing treatment which, considered alone, forms no part of the present invention and requires no specific description here, suitable methods of galvanizing and sherardizing being well known in the art. Assuming that in this instance the sheet iron has been galvanized, the next step is to apply to it a solution of antimony trichlorid in a light mineral oil distillate, such as kerosene, the solution most desirably containing about three quarters of a pound of pure anhydrous antimony trichlorid crystals per gallon of ordinary commercial kerosene of good grade, or about a 10 per cent antimony trichlorid solution in kerosene. This is approximately a saturated solution of antimony trichlorid in kerosene and it is characterized by a bluish pink or purplish color. The content of combined antimony is around 5 per cent. The particular manner of applying this solution to the galvanized iron is not material, generally speaking. The solution may be brushed or sprayed on the galvanized iron, for example; or the galvanized iron may be dipped into the treating solution. Good results can also be obtained by bringing vapors of the solution into contact with the surface to be treated, the antimony salt being carried by the vapors in sufficient quantity to produce the desired plating effect. Where this method is used, vaporization of the solution may be hastened by application of moderate heating.

Whatever method of application is employed, it is unnecessary to apply heat to the metal surface being treated in order to bring about the reaction by which the desired deposit of antimony is obtained on the galvanized iron surface. This reaction takes place very rapidly at ordinary room temperature merely upon contacting the solution with said surface. Progress of the reaction is indicated by a distinct darkening of the galvanized iron surface which becomes almost black after contact with the solution for a short time, that is for a few seconds or minutes. In practice it is sufficient simply to dip the galvanized iron into the treating solution and withdraw it therefrom immediately or after a few moments, after which the treated

metal sheet may be allowed to dry either with or without removing the excess treating solution from its surface by washing with kerosene or with water. In some cases it is found good practice to rub or brush the sheet metal surface vigorously while it is wet with the treating solution, but in most cases this is not essential to the attainment of satisfactory results. Moreover where a burnished surface is wanted, the treated metal sheet may be rubbed or brushed after it is dry, if desired, but this is not essential to the broad invention.

Where desired, the deposit may be produced by electroplating methods as distinguished from the simple dipping operation above described.

The dark colored protective metal coating obtained in the manner above set forth is tenaciously adherent and extremely uniform in character, completely covering the original metal surface in a continuous film of great uniformity and protective power. It adds greatly to the life of the metal sheet, being much more inert and resistant to corrosive influences than either the zinc of the galvanizing coat or the underlying iron. This makes it possible to employ the treated sheet metal in many situations where it is exposed to corrosive liquids or gases that would rapidly destroy galvanized iron not treated in accordance with the present process. For example, the protected metal resulting from the new process can be exposed for long periods of time to sea air, or even to sea water or other salt brines without substantial deterioration, as contrasted with the very rapid corrosion and destruction of ordinary untreated galvanized iron under similar conditions.

It is believed that the dark colored protective film coating obtained as above described is chiefly or entirely metallic antimony; but whether it be metallic antimony or partly an alloy of antimony with the underlying metal is not material to the present discussion since the protective effect obtained is in any event pronounced and utilizable in the practical art in a wide variety of ways. Therefore, in referring herein to the protective metal coating obtained by the process of the invention, it is to be understood that this language is used in a broad sense to include also an alloy of the protective metal with the underlying metal base if in fact this is actually formed to a greater or less extent.

It has also been found that providing galvanized iron with an antimony film coating in the manner above described not only greatly increases the resistance of the galvanized iron to corrosion, but it also has the effect of enabling paint to adhere directly to the surface thereof, whereas heretofore it has been necessary, in applying paint to galvanized iron and steel, to apply first a coat of sizing

in order to render the paint coating properly adherent with the permanency demanded by such conditions as those to which metal sign-boards and the like are exposed in use. Thus, the invention is applicable with great advantage to the treatment of previously manufactured galvanized sheet iron in the construction of sign-boards and the like, the present novel treatment of the sheet metal for this purpose being simply substituted for the usual sizing operation with the two-fold effect not only of ensuring permanent adherence of the subsequently applied paint coat but also of greatly prolonging the life of the sign-board.

The treatment of galvanized sheet iron for sign-boards by the process of the invention is of course merely typical of many uses to which the invention may be put. Thus, other manufactured articles and materials commonly made of galvanized iron or steel, such, for example, as gutter pipes and spouting, wire fencing, barbed wire, and iron and steel wire generally, can be made very resistant to rust and other forms of corrosion to which they are commonly subject by the simple and rapid treatment above described whereby they are provided with a protective antimony coating. The comparative rapidity with which these various manufactured articles of ordinary galvanized iron often corrode and otherwise deteriorate in use, especially where exposed to weather in air contaminated with industrial gases, for example, is well known. The protective film of antimony superposed on the zinc gives a composite protective coating which is resistant to such destructive agencies and gives the protected metal a much longer life than ordinary galvanized metal.

In the foregoing specific example, reference has been made to the use of pure anhydrous antimony trichlorid crystals because this form of antimony trichlorid is for various reasons the most desirable to employ. So-called "butter of antimony", or other commercial form of antimonous chlorid that is sufficiently low in moisture content to enable it to dissolve sufficiently in the non-aqueous solvent employed may be used, but generally speaking they are less desirable than the pure anhydrous crystals because of the greater likelihood that free hydrochloric acid will be present in the treating operation. The fact that the solution is substantially without content of free hydrochloric or other acid corrosive to the surface to be protected is an important and advantageous characteristic of non-aqueous solutions of the type most desirable for use in practicing the present invention.

Neither is it to be inferred that the invention is confined to the employment of antimony trichlorid or other antimony compound. While antimony trichlorid offers

special advantages and is preferred, compounds of other metals soluble in non-aqueous solvents may be employed and analogous effects obtained. Thus, resinates or oleates of other relatively corrosion-resistant metals such as copper and lead, for example, are soluble in various non-aqueous solvents such as hydrocarbon oils, for instance, and can be similarly used.

The employment of a light hydrocarbon solvent such as kerosene is to be particularly recommended, but this specific type of non-aqueous solvent is not essential in the broader aspects of the invention. Thus, assuming the use of antimony trichlorid, solutions thereof in benzol, acetone, amyl acetate, or ethyl acetate, or in mixtures of such of these as are miscible, have been found to function in a manner similar to the kerosene solution hereinabove described. Benzol is especially suitable as it will take up as much as two and one-half pounds of anhydrous antimony trichlorid per gallon. This strong solution may be diluted, as is frequently desirable, with more benzol or with kerosene.

Instead of applying the treating solution to a metal body that has already been provided with a protective coating, as by galvanizing, it is feasible and in many cases desirable to apply it directly to the unprotected metal. Thus, ordinary iron or steel sheets, wire, bars, and other articles, may be provided with a resistant protective coating of antimony by direct application of non-aqueous solutions thereof. The action at ordinary room temperature is usually somewhat slower, however, than where the iron has been first galvanized.

Not only does the use of a non-aqueous solvent permit more ready deposition of the protective metal from solution, but furthermore it makes possible the employment of salts, such as antimony trichlorid, that are insoluble in water except with the aid of strong acids, alkalis or other special assisting agent. The term non-aqueous is not to be construed too narrowly, the presence of such slight amount of moisture in the solution being permissible as will not cause hydrolyzation and resultant deposition of basic compounds therefrom.

What I claim is:

1. The process of protecting metal surfaces against corrosion which comprises depositing antimony on such surface by contacting therewith a solution of antimony trichlorid in a hydrocarbon solvent thereof.

2. The process of protecting metal surfaces against corrosion which comprises depositing antimony on such surface by contacting therewith a solution of antimony trichlorid in kerosene.

3. The process of protecting galvanized iron from corrosion which comprises apply-

ing thereto a solution of antimony trichlorid in kerosene.

4. The process defined in claim 1, further characterized by the fact that the operation is conducted at ordinary temperatures.

5. The process defined in claim 3, further characterized by the fact that the operation is conducted at ordinary temperatures.

6. The process of protecting against corrosion metal surfaces electropositive to antimony group metals which comprises depositing on such surface a metal of the antimony group from a solution of an antimony group metal compound in a hydrocarbon solvent thereof.

7. The process of protecting against corrosion metal surfaces electropositive to antimony group metals which comprises providing such a surface with an adherent protective coating containing a metal of the antimony group by contacting with said surface a solution of an antimony group metal salt in a substantially non-aqueous liquid solvent thereof until said coating is formed, said solution being substantially without free acid content corrosive to said surface.

8. The process of protecting against corrosion metal surfaces electropositive to antimony which comprises providing such a surface with an adherent protective coating containing antimony by contacting with said surface a solution of an antimony salt in a substantially non-aqueous liquid solvent thereof until said coating is formed, said solution being substantially without free acid content corrosive to said surface.

9. The process defined in claim 8, further characterized by the fact that said solution contains at least about 5 per cent of combined antimony.

10. The process of protecting zinc-covered metallic surfaces against corrosion which comprises contacting such a surface with a solution of an antimony salt in a substantially non-aqueous liquid solvent which is mainly hydrocarbon in character until said surface is provided with an adherent protective coating containing antimony, said solution being substantially without free acid content corrosive to said surface.

11. The process defined in claim 10, further characterized by the fact that the solution employed contains at least about 10 per cent of antimony trichloride.

12. The process of protecting against corrosion metal surfaces electropositive to antimony which comprises applying to such a surface a solution prepared by dissolving anhydrous antimony trichloride crystals in a non-aqueous solvent, said solution being substantially without free acid content corrosive to said surface.

13. The process defined in claim 6, further characterized by the fact that the solvent employed comprises benzol.

14. The process defined in claim 10, further characterized by the fact that the solvent employed is mainly benzol and that antimony chloride is dissolved therein.

15. The process defined in claim 7, further characterized by the fact that the solvent employed comprises an aliphyl acetate.

16. The process defined in claim 7, further characterized by the fact that the solvent employed comprises amyl acetate and that antimony chloride is dissolved therein.

In testimony whereof I hereunto affix my signature.

ARTHUR ARENT.

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