

UNITED STATES PATENT OFFICE

2,073,783

METHOD OF CORROSION PROTECTION

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No Drawing. Application September 14, 1935,
Serial No. 40,629

2 Claims. (Cl. 148—4)

This invention relates to a method of protecting from corrosion corrodible metals, such as steel and the other ferrous metals. The following constitutes subject-matter divided from application Serial No. 753,526, filed November 17, 1934, entitled Coating composition.

It is desirable in all instances to protect the surface of metals such as the ferrous metals against corrosion between the period of the rough shaping of the metal and the final finishing treatment. Particularly in the case of tubes, bars, sheets, and the like of steel which are subjected to a galvanizing, or other coating treatment, or which are to be subjected to a cold-rolling or cold-drawing operation, a relatively great length of time may intervene between the initial shaping of the metal and the galvanizing or other finishing operation. If during this period of time the surface of the metal is exposed to corrosion, the pitting of the surface may well become such as is removable with difficulty by pickling, blasting, or other operations which may be performed preliminary to galvanizing, cold-drawing, cold-rolling, or the like. The fact that the surface of the shaped steel carries mill-scale, expedites rusting, and intensifies the destructive effect of the rusting.

Aside from the difficulty encountered in eliminating rust and pitting, there is a substantial loss of metal due simply to the oxidation of surface metal into the form of rust. If metal sheets or bars, and particularly sheets and structural shapes, be allowed to remain unprotected for the relatively extended period which normally intervenes between their initial shaping and their final treatment, the loss of metal due to rusting may amount to 6%, or more, of the initial weight of the metal.

Frequently the rusting of the metal proceeds to such degree, that it is impossible to clean the shape in such manner that it may be successfully galvanized or otherwise permanently coated. There is a loss, therefore, not only in metal destroyed by oxidation, and an increase in the labor necessary preparatory to galvanizing or other finishing treatment, but in extreme instances of rusting the entire preliminary work upon the metal is lost and the shape must be scrapped.

I am aware that various methods have been used temporarily to protect the surface of sheets, bars, and the like, from oxidation in the period between the initial shaping of the metal and the galvanizing, or other finishing, treatment to which the shape is to be subjected. Prior methods of protecting the surface of the metal

consist in painting, varnishing, lacquering, or phosphating the surface. Of these, all save the phosphating process, necessitate removal by an alkali treatment, or solvent treatment, before the stock may be subjected to the application of a permanent coating, or other finishing treatment. An alkali treatment, or a solvent treatment, is a definitely added step in the treatment of the stock, and as such increases production costs.

The oxidation of paints, varnishes, lacquers, and the like, on the surface of the metal, occurring during the period between the application of such temporary protective coating and its removal, renders its complete removal so difficult that there frequently remain on the surface of the metal, after a removal treatment, areas still carrying a deposit of the coating composition, or some of its constituents. Such coated areas, of course, detract substantially from the completeness and value of the galvanizing treatment, since any break in the close adhesion of a galvanized coating tends to the rapid destruction of the metal presumably protected by the coating.

The phosphate process, utilizing generally a manganese phosphate, acts to produce by reaction with the metal to be protected a relatively thin layer of ferric phosphate. This layer must be laboriously removed prior to galvanizing or plating, since its presence on the metal prevents good galvanization of the stock.

It is, of course, necessary in order that a temporary coating be of value that it should not be freely soluble in water, and that it should not, to any great degree, hydrolyze. I have solved the problem both of protection for the metal, and removal of the coating, by producing a coating which is insoluble in water, and which does not hydrolyze readily; but which is readily removed by highly dilute solutions of the mineral acids. It is well-known that, as various stock comes from a hot mill, it inevitably carries a substantial amount of scale, which scale has been referred to above as increasing the tendency toward rusting of the stock. It is the usual practice to subject the stock, whether it be in the form of bars of any cross-sectional contour, tubes, sheets, or plates, to a pickling bath before the shaped metal is coated permanently by galvanizing or the application of some other protective coating, or before it is subjected to a finishing treatment such as cold-rolling or cold-drawing.

The composition of a pickling bath, as used in the steel industry, is a solution of sulphuric acid, usually a seven per cent. solution, used at a tem-

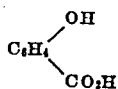
perature of about 150° F. It should be emphasized that the pickling of the shaped ferrous metal in a bath of this nature is not only a well-known, but substantially an inevitable, step in the production of fine finished stock. My coating is of such nature that it is wholly removed during the normal pickling of the metal to which it has been applied. It may further be noted that my coating is removed so rapidly in the pickling bath that it does not add substantially to the duration of the pickling treatment for the removal of scale.

The fundamental ingredient of my coating composition is a product obtained from the reaction of a metallic compound with an organic chemical containing the hydroxyl (OH) radical, which is an acidic aromatic compound of either the phenol, or phenolic, series. It can be stated generally that practically all members of the phenol, and phenolic series are suitable for my purpose. The type of metallic compound should desirably be such as will react with the acidic aromatic under practical reactive conditions. Since the phenol and phenolic compounds are of relatively weak acidity, the metallic compound should desirably be of the more readily decomposable type such as the oxide, hydroxide, or carbonate, of the metal. Certain organic salts of the metals, such as the acetates, may with advantage be used for my purpose.

The theory of my invention is to produce a product either of substitution, or addition, with the phenol, or phenolic, compound, which product possesses certain resin-like qualities rendering it suitable for use as the film-forming ingredient of a temporary coating composition.

Among the aromatic acids, there is a type of acid in which the acidic hydroxyl (OH) radical is attached to a carbon atom to which no atom of oxygen, other than that comprised in the hydroxyl, is attached. These are known as phenols, whether they contain one, or more, hydroxyls. For example, the cresols, or cresylic acids, are phenols, as are the xylenols and the specifically named phenols. The naphthols, in which the naphthalene double ring replaces the benzene ring, are also phenols. These all, as stated, are suitable for my purpose.

I may also use as the organic basis of my compound, one of the phenolic acids. These are aromatic acids, which contain both the carboxyl (COOH), and also contain the hydroxyl in the same acidic relation as do the phenols. For example, I have successfully used salicylic acid, or ortho-hydroxyl-benzoic acid:



For reasons of economy, I prefer to use such simple phenols as phenol proper, cresol, xynol, naphthol, and their homologues. With one or more of these organic compounds, I react a compound of a metal.

Among the metals, only those lower than antimony in the electromotive series need positively be eliminated. This is primarily because of the fact that they are relatively so inert. It is a fact, however, that the highest member of the electromotive series cannot desirably be utilized by themselves to react with a phenol, or phenolic acid, to produce a film-forming ingredient for my coating composition. The compounds produced by reaction of a phenol, or phenolic acid,

with potassium, sodium, or the theoretical metal ammonium, are quite soluble in water, and would, therefore, give but evanescent protection against oxidation of a metallic surface. Barium, strontium, and calcium, tend to produce products of addition, rather than substitution, with the phenols and phenolic acids. The compounds obtained by reaction with them are, therefore, of high melting-point. Such compounds are also somewhat soluble in hot water.

The products of reaction of these metals with a phenol, or phenolic acid, may suitably be used in admixture with a product of reaction between a phenol, or phenolic acid, and one of the metals lower in the electromotive series than calcium. Thus, I have used, as a film-forming mass, a mixture of calcium cresylate and lead naphtholate. It is probable that reaction products of the phenols, and phenolic acids, with barium or strontium might similarly be used.

It is preferable to use, for reaction with a phenol, or phenolic acid, a compound of one of the metals lower in the electromotive series than is calcium, if the aromatic compound of such metal is to be used alone as a film-forming ingredient. Of the metals lower than calcium, however, it should be noted that the compounds of zinc and magnesium have approximately the solubility of calcium. The reaction product of these metals is, therefore, preferably not used by itself save when the product results from the reaction of zinc, or magnesium, with one of the organic reagents of higher molecular weight, such as naphthol, or a phenolic mixture in which the higher molecular weight reagent, such as naphthol, predominates.

For use in the temporary protection of ferrous metal from rusting, I find that a highly reactive lead compound gives ideal results. This is for the reason that in a pickle bath one product of reaction between the organic lead compound and the sulphuric acid of the bath is the insoluble lead sulphate, which, being heavy, falls to the bottom of the bath. Antimony sulphate is unstable, and acts to regenerate sulphuric acid and to produce the insoluble, but flocculent, hydroxide of the metal. Care must be taken in its use to prevent adherence of this precipitate to the surface of the metal which has been pickled to a clean, bright condition. The same is true of tin.

Returning to the organic constituent of my material, I have reacted phenol, cresol, xynol, naphthol, and salicylic acid, which are the commercially available phenols and phenolic acids, with lead oxide to obtain a mass having resin-like qualities. It may be noted that amyl-phenol (para-amyl-tertiary-phenol) may be obtained commercially, and may be used, but is of relatively high price.

The reaction product of lead oxide with phenol has the disadvantage that it is somewhat susceptible to hydrolysis, and to a lesser extent the reaction product with cresol is susceptible to hydrolysis. Lead compounds of xynol and naphthol have practically no tendency to hydrolyze. Naphthol has a melting-point so high that it tends to lessen the adhesive qualities of the compound, produced by its reaction with the metal. A combination of cresol and naphthol is wholly satisfactory, since the inclusion of naphthol decreases the tendency of the combined chemicals to hydrolyze to a point at which such tendency is not practically disadvantageous, while the combined melting-point is sufficiently lower than the

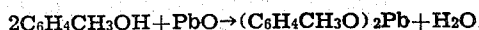
melting-point of the naphthol compound to secure good adhesion.

It may be generally stated that among the stated organic compounds and their homologues, suitable combinations may readily be made to meet the conditions of use to which the coating composition is to be put, simply by bearing in mind the relative tendency of the compounds to hydrolyze and their relative melting-point, without conducting any extended series of experiments. As a guide, it may be stated that by using as the organic constituent of my material 60% by weight of naphthol to 40% by weight of cresol, I have obtained by reaction with lead oxide a film-forming material which in use, as hereafter described, wholly protected a ferrous surface to which is was applied for a period in excess of three months, without any appreciable deterioration occurring from hydrolysis, although the coated metal was stored in a location exposed to moisture.

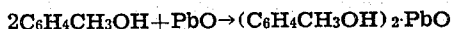
As a typical example of the production of the organic-metal compound, a mixture of cresol and naphthol was fused, and lead oxide was introduced slowly in solid state, and divided form, with agitation. Throughout the reaction the temperature was maintained adequate rapidly to drive off water evolved by the reaction, and was maintained below that point at which volatilization of the organic reagents would occur. In this reaction I have found a temperature of approximately 320° F. suitable, and have maintained such approximate temperature throughout the reaction.

It should be explained that the lead oxide, or other metal compound, desirably is not included to the full amount based on its combining weight and valency. This is for the reason that, if included up to the full amount, the resulting product is of lessened solubility in hydrocarbon solvents. It is desirable that the lead oxide should be included in a percentage not substantially less than 90% based on its combining weight and valency, since the resultant product exhibits some tendency to hydrolyze, if the actual content of the metal is substantially less than 90% of the theoretically complete reaction between it and the organic chemicals. I have found that an inclusion of lead oxide in a quantity equal to 95% its theoretical combining weight and valency, is suitable. Formulae for the reaction may be given as follows:

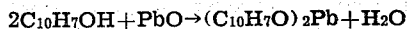
(A) Cresol and lead giving "lead cresylate" and water



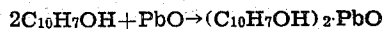
B) Cresol and lead giving additive compound



(C) Naphthol and lead giving "lead naphtholate" and water



(D) Naphthol and lead giving additive compound



I am certain that a large proportion of the reaction occurs in accordance with formulae A and C. This is because of my observation of a relatively great quantity of evolved water, which proved to be approximately 90% of the theoretical water product of the reactions. There is no available literature as to this type of reaction.

Although the exact nature of the reaction is

theoretical, I am led, as mentioned above, to the belief that it is substantially wholly in accordance with the formulae A and C. As noted above, in reacting a calcium compound with a phenol, or phenolic acid, the tendency is to produce to a greatly increased degree additive compounds. In accordance with the type of the reactions B and D. It may be noted that the additive compounds are less resin-like in their qualities than the substitution products. The same is true of barium and strontium.

The resultant product of reacting the lead oxide, and also the other compounds of lead and the metals adjacent lead in the electromotive series, with the phenols is a mass which has film-forming qualities of the general nature found in the resin-oil varnish bases, but which has the property of rapid decomposition in the presence of mineral acids, even in relatively high dilution. This material is soluble in the usual coal tar distillate solvents and in mixed coal tar and petroleum distillate solvents.

I have made up various grades of my coating composition by dissolving various specimens of my special film-forming material in mixed solvent from a proportion of 20% by weight of the film-forming material to 60% by weight of the film-forming material. The latter proportion is, for the specific material formed in the above example, the maximum content of film-forming material in the solvent which gives a flowable composition. I have found that a coating composition comprising 35% by weight of my special film-forming material and 65% by weight of a combined mixed solvent, when spread upon the surface of steel as shaved in a hot mill, adequately protects the metal for a period of at least three months.

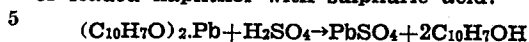
The solution of my special film-forming material may be made by cold-cutting, if so desired. It is convenient, however, to dissolve the material in the solvents, immediately upon completion of the reaction between the organic reagents and the metallic compound used, as evidenced by cessation in the evolution of water from the reaction mixture. The coating composition, or solution, may be applied in any suitable manner as by spraying, dipping, brushing, or spreading.

When steel shapes, protected by my coating composition, are introduced into a pickling bath of the nature above-mentioned, it has been found that the temporary coating is removed in from 1 to 3 minutes after the introduction of the metal, exposing the surface of the metal to the action of the pickle for the removal of mill-scale and brightening of the metal in accordance with the usual functioning of a pickle bath. There remains on the metal after pickling no trace of the coating composition.

It has been above noted that my special film-forming material, as produced by the reaction of a lead compound with one or more of the phenols, or phenolic acids, decomposes to produce by reaction with the sulphuric acid of the pickling bath an insoluble lead sulphate, and that this insoluble product of the reaction of the pickling bath is precipitated to the bottom of the pickle vessel as is also, in substance, the organic component, or components.

In explanation, it may be mentioned that, in accordance with the formulae which I consider the more accurate as illustrating the chemical composition of ingredients in my special film-forming mass, the acidic aromatics are reformed

by reaction with the sulphuric acid, in the formation of the lead sulphate. This may be illustrated by the following formula relating to the reaction of leaded naphthol with sulphuric acid:



While most of the organic acid is precipitated, as explained above, a relatively small percentage is taken into solution in the pickling bath. This small percentage of organic acid serves as an inhibitor, to modify the reaction of the bath in attacking the actual metal exposed by the removal of scale. It thus exerts a positively beneficial, rather than a detrimental, effect in the pickling bath. It should be emphasized that the protection of the surface of a highly corrosional metal, such as steel, in the intervening period between its shaping and pickling, is of great importance. By protecting the surface of the metal during this period, and thus preventing the formation of rust, a smoother plating with metals such as tin, chromium, and the like, is obtained, since progressive pitting of the metal is prevented. A galvanized surface of the metal is also smoother, when permanently protected by galvanizing, due to the absence of deep pitting, and the like, and, when hot galvanized, the galvanized coating is brighter and more uniform, showing a clear spangle. Due to the absence of surface defects, a more uniform and homogeneous permanent coating may be applied to the metal, whether it be galvanized, or whether it be plated with any of the protective metals.

With these advantages, arising from the temporary protection of steel surfaces prior to the application of a permanent protective coating, in mind, it should be appreciated that my coating composition has rendered such protection feasible commercially. Previous coatings being either so soluble, or so subject to hydrolysis, that they were inefficient, or of such nature as to render their removal difficult and uncertain, it has been preferred to permit rust to form upon the steel rather than to protect it by a paint or varnish. My coating composition, since it both gives adequate protection and is readily removable, presents no problems which might inhibit its universal use. It is to be noted that the only added step, in the treatment of the metal, involved in the use of my coating, is the mere application of the coating, since its removal occurs in a step normally incident in the treatment of steel.

Quite obviously the protective coating may be removed from the steel by dipping the steel into an acid bath in immediate preparation for its introduction into the pickling bath proper. Also the mineral acid of such bath may be of a concentration greater than that employed in actual pickling. The employment of a two-stage bath, while unnecessarily complicating the pickling operation, clearly falls within the scope of my invention. Also the use of a preliminary, coating-removing bath, the acid of which is more concentrated than is necessary for adequately pickling the steel, is without advantage, since removal of the protective film is instantly effected by an acid solution of the concentration normally employed in pickling. As used in the claims, the terms "dilute acid" and "pickling bath" are therefore to be read as terms of description and not of limitation.

Incidentally, it may be noted that my coating composition is substantially colorless, and

that it will retain the color of the usual pigments. It may thus be colored in accordance with the stock to which it has been applied, either to identify a customer to whom the stock is to be delivered, or for any other purpose of identification or classification.

Also the pigmented composition may, if desired, be used on stock, not necessarily protected from corrosion, by applying it simply as a paint or stencil composition to give identification of the stock as to origin, grade, shipment, or the like. As so used, the ready removability of the composition in a pickling bath is similarly of great advantage.

It should be explained that by reacting a compound of any one or more of the metals, in accordance with the explanation and limitations above given, with any one or more of the phenols, such as phenol, cresol, xyleneol, or naphthol, a compound is obtained which is sufficiently insoluble in water to give temporary protection to a surface for some period of time and under some conditions. The same is true as to compounds of one or more of the metals with the homologues of phenol, cresol, xyleneol, and naphthol, and with the phenolic acids.

In the specification, I have previously disclosed factors which enable one skilled in the art to produce most readily and economically the variants of my temporary coating composition suitable and adequate for various conditions of use. In making such detailed disclosure it has not been my intention to limit the invention, to any special metallic compound or compounds, or to any special organic acid or acids, responding to the definition of a phenol or phenolic acid. A chemist skilled in the art will, as noted above, be able to use to advantage for the protection of metal or some other material, for some period of time, each of the compounds considered by me as workable. Such description as points out the tendency of certain of the compounds to hydrolyze, for example, is not intended herein as excluding such compounds from consideration in a protective coating for any purpose, but such description is to be considered as instruction to the art as to the practical advantages and limitations of the several of the possible compounds, thus giving a guide to the art, which permits optimum advantage to be obtained from my invention.

Thus, I have in the foregoing specification criticized phenol, as the organic chemical to be reacted with a metallic compound, for the reason that it is relatively subject to hydrolysis. This acid may, however, be reacted with a metallic compound to protect a surface for a relatively short period of time. The like is true of cresol as reacted alone with a metallic compound. In the specification I have criticized xyleneol and naphthol, as producing by reaction with a metallic compound, a product which is deficient in adhesion. None the less, a mass obtained by reaction with these latter phenols, may be used upon surfaces of a nature to facilitate the adhesion of a coating. As applied to surfaces other than metallic surfaces, the possession of adhesive qualities in lesser degree may work no disadvantage.

Similarly I have stated that the more reactive compounds of the metals should desirably be used, because of the relatively weak acidity of the phenols and phenolic acids. By this I do not intend to state that other, less reactive, com-

pounds may not, by care and patience in conducting the reaction, successfully be used.

Finally it should be noted that, in the disclosure of the specification, it is pointed out 5 which metals give desirable compounds for reaction with the phenols and phenolic acids. So many metallic compounds may be used, either by themselves or in association with other metallic compounds, to make variants of my coating 10 composition that, with the guides comprised in the specification, it becomes wholly proper to utilize in the claims, as defining my coating composition generally, the term "metal compound."

15 It has been noted that the phenols proper and the phenolic acids have in common the characteristic that in them a hydroxy radical is attached to a carbon atom to which no oxygen other than that contained in the hydroxy group is 20 attached. This characteristic, common both to phenols proper and to phenolic acids, is the "phenolic" type characteristic. As the term "phenolic substance" is used in the following claims, it is intended by it to embrace both 25 phenols proper and phenolic acids.

I claim as my invention:

1. The method herein described of producing shaped and protectively coated steel which comprises shaping the steel in conventional manner, 30 temporarily protecting the shaped steel by applying to the surface of the steel a continuous impervious and adherent integument proof against

water and subject to disintegration by reaction with mineral acids, in pickling the steel disintegrating and completely removing the temporary impervious integument by chemical reaction of the pickling acid therewith, thereby to impart 5 to the steel a clean bright surface which is in preparation for the application of an ultimate coating thereto wholly free of the temporary protective integument, and in conventional manner effecting permanent protective coating of 10 the shaped and pickled steel.

2. The method herein described of producing shaped and protectively coated steel which comprises shaping the steel in conventional manner, temporarily protecting the shaped steel by applying to the surface of the steel a continuous 15 impervious waterproof and adherent integument consisting in substantial entirety of a film-forming metallic compound of a phenolic type hydroxy-aromatic hydrocarbon substance, in pickling the steel disintegrating and completely removing the temporary impervious integument 20 by chemical reaction of the pickling acid therewith, thereby to impart to the steel a clean bright surface which is in preparation for the application of an ultimate coating thereto wholly free of the temporary protective integument, and in conventional manner effecting permanent protective coating of the shaped and pickled 25 steel. 30

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