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MATERIALS FOR AND METHODS OF TREAT-
ING METALLIC ARTICLESAllan E. Chester, Shaker Heights, Ohio, assignor
to Ferro Enamel Corporation, Cleveland, Ohio,
a corporation of OhioNo Drawing. Application December 21, 1936,
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This invention relates as indicated to materials for and methods of treating metallic articles and pertains more particularly to the treatment of metallic articles such as, for example, steel sheets, wires, bars, rods, castings, forgings, and the like, by certain named organic materials for the purpose of either cleaning the same or applying thereto a coating particularly effective to prevent oxidation and staining of the work under certain conditions.

It is a principal object of this invention to provide materials for and methods of treating metallic articles such as those named in order to remove therefrom soluble films such as grease or dirt, which methods, due to the employment of particular materials previously not used for this purpose are characterized by low cost of operation and the attainment of superior results.

It is another object of this invention to provide materials for and methods of applying a film to metallic articles such as sheets, which film is particularly effective to protect the work from oxidation and staining and which film may, if desired, be readily removed from the work prior to subjecting the work to a coating or forming operation, although the nature of the film is such that it need not be removed prior to most forming operations.

Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means and steps hereinafter fully described and particularly pointed out in the claims; the following description setting forth in detail certain means and modes of carrying out the invention, such disclosed means and modes illustrated, however, but few of various ways in which the principle of the invention may be used.

This invention may be broadly stated as comprising the treatment of metallic articles such as ferrous metallic sheets, bars, wire, rods, forgings, castings and the like by means of halogenated or more specifically chlorinated, saturated hydrocarbons having a boiling point above 100° C. and preferably above 130° C.; the invention being characterized by the use of particularly named chlorinated saturated hydrocarbons in carrying out certain more particularly defined methods of treating the work.

Materials useful in this invention

Among the halogenated or more specifically chlorinated saturated hydrocarbons which have been found useful in practicing this invention

are the halogenated or more specifically chlorinated pentanes, such as monochlor pentane, dichlor pentane, trichlor pentane; the halogenated or more specifically chlorinated butanes, such as monochlor butane, dichlor butane and trichlor butane; and the halogenated or more specifically chlorinated hexanes, such as monochlor hexane, dichlor hexane and trichlor hexane.

Of the above-named specific examples, dichlor pentane is preferred on account of its more general availability at a lower cost and furthermore, its general superiority of effectiveness in carrying out the processes comprising this invention.

Due to the fact that there is usually, either intentionally or accidentally, a certain amount of water present under the conditions under which the previously named halogenated or more specifically chlorinated saturated hydrocarbons are employed in treating ferrous metallic articles, such chlorinated materials will hydrolyze to a certain extent, forming hydrochloric acid which attacks both the work, as well as the apparatus used in carrying on the process. For certain types of processes contemplated by this invention, this hydrolysis is preferably reduced to a harmless minimum and this may be accomplished by the employment with such halogenated or more specifically chlorinated saturated hydrocarbons of minor percentages on the order of upwards of one-half of 1% of a suitable stabilizer or inhibitor.

It has been found that diamylamine is particularly effective as a stabilizer and inhibitor for use with the above named halogenated or more specifically chlorinated saturated hydrocarbons, particularly when dichlor pentane is employed.

It is within the contemplation of this invention to employ instead of the above-named stabilizer and inhibitor, monoamylamine, triamylamine, as well as such conventional stabilizers and inhibitors as are or may be employed for the purpose stated in conjunction with the specified type of chlorinated saturated hydrocarbons.

The method of cleaning metals

One of the processes comprised by the present invention has been designed for the purpose of removing films of oil or grease from metallic articles such as ferrous metallic sheets and such process comprises the following steps performed in substantially the order stated:

The work to be treated is immersed in a liquid or vapor bath of the selected chlorinated saturated hydrocarbon such as dichlor pentane and

it will be found that best results will be secured if the bath is maintained at an elevated temperature ranging between room temperature and the boiling point of the particular solvent.

- 5 In this bath all of the grease and oil film adhering to the work will be removed by the solvent action of the chlorinated saturated hydrocarbon.

The next step in the process depends largely upon the use to be made of the work which has been treated in the first step. If the work is to be plated, galvanized or permanently rust-proofed, etc., it will be found desirable to remove from the work the film of halogenated or more specifically chlorinated saturated hydrocarbons such as dichlor pentane adhering thereto after the work has been removed from the bath described in connection with the first step of the process.

The film of the halogenated or more specifically chlorinated saturated hydrocarbon such as dichlor pentane may be conveniently removed from the work by immersing the latter in a weak, aqueous, alkaline bath which may have dissolved therein from about three to about six ounces per gallon of the following composition:—

Sodium hydroxide	from about 20% to about 40%
Sodium orthosilicate	from about 30% to about 60%
Tri-sodium phosphate	from about 5% to about 15%
Sodium gluconate	from about 5% to about 10%
Tri-ethanolamine	from about 1% to about 3%

- 30 The above described alkaline cleaning bath will, for most efficient results, be preferably operated at a boiling temperature.

The action of the cleaning bath may be considerably facilitated by passing electric current through the work and when direct current is used, the work should be in the cathodic position.

For certain types of work and in certain processes, the omission of the inhibitor or stabilizer from the chlorinated saturated hydrocarbon bath may be found desirable for certain results. As above indicated, the omission of the stabilizer results in the production of increased amounts of hydrochloric acid. It has been found that if the stabilizer or inhibitor is omitted, the amount of acid thus formed in attacking the work, particularly certain types of metallic sheets, will result in the production of a surface condition on the sheets which is particularly desired; for example, when the sheet or similar article thus treated is to have certain types of finishes such as porcelain enamel applied thereto.

If the stabilizer or inhibitor is omitted, however, care should be exercised in the selection of the material from which the work handling apparatus is formed so that the hydrochloric acid generally, even though very slight, will not ultimately result in the destruction of such handling apparatus.

Process for producing anti-oxidizing film

60 In present-day steel mill practice, it frequently happens that metal sheets, after being pickled and scrubbed to remove all foreign material from the surface thereof, are stored for a relatively short period before being further processed. With the metallic sheet thus carefully cleaned, the surface thereof is subject to oxidation and consequent staining at a very rapid rate unless some means is provided for protecting the surface of the sheet from the atmosphere. Hydrocarbon mineral oil and similar materials are currently being applied to clean sheets in order to exclude the atmosphere therefrom; however, such practice is objectionable in that a relatively expensive operation must usually be resorted to

in order to remove such film before the sheet can be further processed.

It is within the contemplation of this invention to apply to cleaned metallic sheets after pickling and scrubbing a film of a chlorinated saturated hydrocarbon such as dichlor pentane, which film has been found to very effectively prevent oxidation and consequent staining of previously cleaned metallic sheets, even though such sheets have been permitted to stand exposed to the atmosphere for appreciable periods of time. The employment of this type of protective coating is advantageous in that it may be readily removed if desired, either by means of the previously described alkaline bath treatment or by merely heating the work to a temperature above the boiling point of the film material to volatilize the same. The nature of the film produced by the dichlor pentane is such that for certain subsequent forming operations of the metallic sheets it is not necessary to take any positive steps to remove the film, since it has been found that the temperatures encountered in such subsequent processing steps are in themselves sufficiently high to drive off the film.

Process to prevent staining

In conventional sheet mill practice, the lapse of time during which the clean sheets are transferred from the picklers to the scrubbers and during which such sheets are in contact with the atmosphere, is usually sufficient to result in an undesired staining of the sheets. It has been found that this undesired staining may be prevented by the application to the sheets of a film such as is formed by an aqueous bath containing from about 2% to about 8% by weight of dichlor pentane which likewise advantageously contains appropriate amounts of an emulsifying agent such as a soap or the like.

In the foregoing description of the method of cleaning metallic articles, it has been stated that the film of halogenated saturated hydrocarbons such as dichlor pentane may be removed from the work in the specified manner, if such should be necessary or desirable prior to the step of subjecting the work to further processing. Since, as above pointed out, however, the adherent film of the hydrocarbon such as dichlor pentane acts as a means of preserving the surface of the work, it is within the contemplation of this invention to permit the film of the halogenated hydrocarbon residing on the surface of the work after the cleaning operation to remain thereon and serve as a protective medium for the clean surface until the work surface is permanently protected by means of the final finish applied thereto, which, as previously indicated, may be a permanent rust-proofing coat, porcelain enamel, etc.

The halogenated saturated hydrocarbons previously referred to and used in the processes comprising my invention may be employed to protect the metal surface against other than the atmosphere.

A specific example of the manner in which the halogenated saturated hydrocarbons such as dichlor pentane may be employed for this last-named purpose is as follows:—

In the process of wire-drawing, the wire, prior to its passage through the reduction die, is led through a lime bath which is employed for the purpose of providing on the wire a thin film of lime which acts as the lubricant as the wire passes through the drawing die. The impurities, as well as alloying ingredients present in the wire usually combine with the constituents of

the bath in the formation of soaps and similar compounds usually dark in color, which, when the wire passes through the drawing die, are smeared on the surface thereof so that the wire, as it leaves the drawing die, possesses a dull finish.

Halogenated saturated hydrocarbons such as dichlor pentane contemplated for use in the processes comprising this invention are not miscible with water and are somewhat lighter than a saturated lime solution so that a layer of the same may be maintained on top of the lime bath through which the wire passes on its way to the drawing die. As the wire passes into the bath, it will first be coated by the halogenated saturated hydrocarbon such as dichlor pentane, which will be effective to prevent reaction between the bath and the surface of the wire so that the previously mentioned objectionable compounds which would tend to discolor the wire are prevented from forming. The film of the hydrocarbon which adheres to the wire does not, however, prevent the adherence thereto of sufficient quantities of lime from the bath so that sufficient lime is present to act as the necessary drawing lubricant.

It is within the contemplation of this invention to maintain the halogenated saturated hydrocarbon in a separate vessel instead of in a film on top of the lime bath and when this expedient is employed, the wire will first be passed through the bath of the halogenated saturated hydrocarbon and then into the lime bath.

Throughout the foregoing description, certain compositions have been given for the various treating baths. It is to be noted that the mentioned constituents are not essentially the only ingredients present; provided, however, that there should be no additional ingredient which is incongruous with the ingredients which have been indicated as essential.

While of the specific examples of the halogenated saturated hydrocarbons which have been given as usable in the processes comprising my invention, the chlorides have been indicated as preferable on account of their low cost and general availability, the bromides, fluorides and iodides are also operable.

The above described invention, it will be noted, is characterized by the employment of dichlor pentane as the preferred chlorinated saturated hydrocarbon for the purposes stated in the particularly described processes. This particular material has, as a result of actual tests, been found to be unusually effective for the stated purposes and its use particularly attractive from an economic standpoint on account of its relatively low cost and general availability.

Other forms may be employed embodying the features of my invention instead of the one here explained, change being made in the form or construction, provided the elements stated by any of the following claims or the equivalent of such stated elements be employed, whether produced by my preferred method or by others embodying steps equivalent to those stated in the following claims.

I, therefore, particularly point out and distinctly claim as my invention:—

1. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film comprising a halogenated saturated hydrocarbon having a boiling point above 100° C.

2. In the process of preserving the surface of

ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film comprising a chlorinated saturated hydrocarbon having a boiling point above 100° C.

3. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film comprising a halogenated saturated hydrocarbon selected from the class consisting of halogenated butane, halogenated pentane and halogenated hexane.

4. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film comprising a chlorinated saturated hydrocarbon selected from the class consisting of chlorinated butane, chlorinated pentane and chlorinated hexane.

5. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film of chlorinated butane.

6. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film of chlorinated pentane.

7. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film of chlorinated hexane.

8. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form the step of maintaining thereon a film comprising a halogenated saturated hydrocarbon selected from the class consisting of halogenated butane, halogenated pentane and halogenated hexane and a stabilizer of the type represented by amyl amine.

9. In the process of preserving the surface of ferrous metallic articles during and subsequent to fabrication into final form, the step of maintaining thereon a film comprising a halogenated saturated hydrocarbon selected from the class consisting of halogenated butane, halogenated pentane and halogenated hexane, and then treating the surface containing such film by means of a weak alkaline bath.

10. The method of cleaning ferrous metallic articles which comprises subjecting the same to a bath of chlorinated pentane to which has been added minor amounts of an amyl amine and then removing the adherent film of such cleaning material by means of a weak alkaline bath which contains minor amounts of tri-ethanolamine.

11. The method of preserving the surface of a clean ferrous metallic article which comprises applying thereto a chlorinated saturated hydrocarbon of the class consisting of chlorinated pentanes, chlorinated butanes, chlorinated hexanes to which there has been added minor amounts of an amyl amine.

12. The method of preserving the surface of a clean ferrous metallic article which comprises applying thereto a film of a chlorinated pentane and an amyl amine.

13. The method of preserving the surface of a clean ferrous metallic article which comprises applying thereto a film of dichlor pentane containing minor amounts of diamylamine.

14. The method of preserving the surface of a clean ferrous metallic article which comprises applying thereto an emulsion containing from about 2% to about 8% by weight of a chlorinated saturated hydrocarbon of the class consisting of

chlorinated pentanes, chlorinated butanes and chlorinated hexanes.

15 The method of preserving the surface of a clean ferrous metallic article which comprises applying thereto an emulsion containing from about 2% to about 8% by weight of a chlorinated pentane.

10 16. In the process of wire-drawing, the steps of successively applying to the wire to be drawn, films of a halogenated saturated hydrocarbon and lime and then drawing the wire through the reducing die.

15 17. In a process of wire-drawing, the steps of successively applying to the wire to be drawn films of chlorinated pentane and a solid drawing lubricant and then drawing the wire through the reducing die.

20 18. In the preparation and preservation of ferrous wire as for reduction by die-drawing, the step of establishing a film of chlorinated pentane on the wire beneath a coating of drawing lubricant, whereby the steel of the wire is protected

from injurious contamination by such drawing lubricant.

19. In the preparation and preservation of steel articles which are to be further processed, the step of establishing a film of halogenated saturated hydrocarbon having a boiling point in excess of 100° C. on the surface of such article beneath a coating applied in such preparation whereby the said surface is protected from injurious contamination by such coating.

10 20. In the working and processing of ferrous articles, the method of preserving a surface thereof between operative steps comprising the application thereto of a film of a halogenated saturated hydrocarbon having a boiling point not below 100° C. and the maintenance of said film until application of a further operative step to such article, whereby such surface is protected from injurious contamination by contacting substances.

20 ALLAN E. CHESTER.