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COATING COMPOSITIONS FOR METALS AND METHOD OF HEAT TREATING METALS

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My invention, having broad application to the metal trades, more particularly concerns the matter of protecting the surface of metal against excessive scaling and other attack during the handling and heat-treating of such metal.

An object of my invention is to provide a method of processing steel products, while protecting the surface thereof from attack under high temperature operating conditions, all without appreciable concern as to the particular composition type or grade thereof, or as to the shape, configuration or size, or the prior treatment or processing of such products, the said method effectively protecting the metal surfaces during such high temperature processing against scaling, chemical reaction, either removal or addition of carbon to the surface of the metal, chromium depletion, and the like.

Another object is to provide a coating composition or formulation for protecting the surface of metals undergoing high temperature treatment, which formulation, low in cost and simple in production and employing commercially available ingredients, is readily applied to a variety of surfaces in a number of different manners, all without pre-treatment of the metal surface and which, thus applied, effectively protects the surface of the metal regardless of the composition, shape, mass or prior treatment of such metal, while displaying enduring high bonding strength both in green and in set condition, which formulation is further characterized by its relative inertness without active participation in surface attack on the metal, its low toxicity, its relative lack of flammability, and its comparatively ready removability from the surface of the metal upon conclusion of the heat cycle.

Yet another object is to provide a variety of products in terms of composition, dimension and configuration, all having in common, however, that for subsequent handling and heat-treatment they have been preliminarily conditioned through the application to the surfaces thereof of thin coatings of protective material, which coatings are flexible, tough and resistant to mechanical abrasion, displaying requisite qualities of physical strength both in green and set condition, and are characterized by relative inertness and freedom from any tendency towards either intergranular penetration of the metal products coated or burn-in on the surface thereof.

All the foregoing, together with many other highly practical objects and advantages, attend the practice of my invention which other objects in part will be obvious and in part more fully pointed out hereinafter.

My invention, accordingly, may be considered to reside in the composition, formulation, and interrelation of materials; in the application of the same to the metal products to be treated; and in the metal products on which such composition or formulation is applied, as well as in the relation of each of the materials or ingredients to and with one or more of the others, the scope of the application of all of which is more fully set forth in the claims at the end of this disclosure.

As conducive to a more ready understanding of my invention, it may be noted at this point in the disclosure that in processing many types of steels, modern-day mill practice commonly includes high temperature heat-treatment. Typical of such steels are those of high carbon content, the alloy steels of both high and low alloy contents, and particularly the various grades and types of stainless steel. Treatment at elevated temperatures illustratively and typically includes not only heat-treatment as in age-hardening certain of the steels, but as well, the annealing of such steels, or the hardening and tempering of others prior to working, forming, or the like.

It has long been recognized that heat-treatment at elevated temperatures is detrimentally characterized by the formation of various oxides on the surface of the metal products, these oxides being known as scale. In point of fact, the formation of scale involves a considerable loss of metal. This is even true of the stainless steels, and especially those relatively low in chromium content. This loss of metal, of course, is accompanied by a corresponding sacrifice of finished surface and of surface detail in the metal products themselves. Close-tolerance compliance to, and retention of, dimensions initially imparted to the products are rendered difficult if not impossible. The foregoing is especially true as concerns batch processing wherein the products, illustratively, rolls of wire, are charged, usually in large numbers, into the furnace. In such batch processing, both from the standpoint of economy and from operating conditions, control of the atmosphere is out of the question. And the furnace atmosphere usually encountered may be either strongly oxidizing or strongly reducing, this to a certain extent depending upon the nature of the fuel and/or the fuel-air ratio.

Quite naturally, therefore, industry has given much study to controlling and minimizing detrimental formation of scale, while otherwise affording requisite protection to the surface of the metal. Despite intensive investigation of this problem over a period of years, however, and despite introduction to the industry of a number of commercially available protective coatings, such proposals as have heretofore been made have in large measure fallen short, in one or more respects, of fulfilling essential minimal requirements of a coating material for service during high temperature heat-treatment practices. And as has been indicated, this is particularly so as concerns processing stainless steel or other high alloy products. For while chemically formed films have been proposed, including black oxide coatings, and while as well refractory oxides, glazes, enamels, paints and the like have been suggested, such films and coatings have only limited application, albeit they sometimes provide adequate protection for the specific purpose for which intended while attending close adherence to prescribed technique.

Illustratively, certain coatings, of which silica dioxide is typical, fail to provide adequate protection, largely because of the comparatively porous nature of the film as dried upon the metal surface. Other coatings fail to display proper adhesion to the metal and/or resistance to damage in the mechanical handling to which the products are necessarily subjected during processing. Some formulations are attended by burn-in of detrimental components of the protective coating into the surface of the metal undergoing treatment. This undesirable phenomenon is observed when employing coatings wherein lead is a constituent. Moreover, where included as an ingredient of

the protection composition, zinc tends to penetrate into the metal surface. In other formulations intergranular chloride attack is encountered. Some coatings, while initially satisfactory, fail to protect the metal products at the elevated temperatures to which they are exposed for required prolonged duration of treatment. Many compositions do not display requisite flow characteristics, stability in the solution of the component elements, or requisite freedom from flammability. Others are difficult of removal. For one reason or another, the known coating materials now commercially available have fallen short of fulfilling the practical demands of industry.

An important object of my invention, therefore, is to provide both a new coating composition or formulation and a method of compounding the same and of applying the same to the products requiring and undergoing protection, which formulation, entirely practical both in composition and in mode of utilization, is comprised of inexpensive materials which are readily available on the market and which, thus compounded, displays requisite stability and easy-flow qualities and is readily applicable to metal surfaces of a variety of forms and dimensions; which coating, thus applied, possesses requisite qualities of physical strength, both in green and dried condition, providing adequate protection to the surface of the metal during prolonged exposure to high temperature in varied furnace atmospheres, and which coating can be removed following completion of heat-treatment in simple manner with but minimum processing.

In the practice of my invention I combine a quantity of refractory inorganic oxides, silicates, chromates or molybdates with a flux, an organic resin, and a volatile vehicle for the whole. Typically, the oxides, silicates, chromates and molybdates may be selected from the group including but not being limited to silicon dioxide, alumina, hydrated aluminum silicate, magnesia, hydrated magnesia silicate, chromium oxide, nickel oxide, iron oxide, titanium oxide, zirconia, barium chromate, lead molybdate and lead chromate. Actually, certain naturally occurring materials may be employed in substitution in whole or in part for the more refined forms just mentioned. Illustrative of these naturally-occurring silicates of aluminum and magnesium may be included clay, kaolin, asbestos, bentonite, talc, pyrophyllites and the like.

Preferably, I employ a combination of finely divided silicon dioxide and one or more of other refractory oxides and silicates, chromates and molybdates. While the added and more refractory inorganic products, either of refined or naturally-occurring type, should also be finely divided, nevertheless they should have particle size somewhat coarser than those of the very fine or nearly colloidal silica. Such gradation of particle size contributes to more intimate bonding of the coating to the metal surface. At the same time, I find the protective film in dried form is less porous than where all particles of the inorganic solid constituents are of the same size. And finally, the colloidal or nearly colloidal silica serves as a suspension agent to keep the other constituents more uniformly dispersed in the liquid formation.

More particularly, in the practice of my invention I intimately admix from 3 to 45 parts by weight of an inorganic substance selected from the group consisting of inorganic oxides, silicates, chromates and molybdates. And with these in powdered form, I provide from 1 to 40 parts of organic resin solids, and from 0.2 part to about 10 parts of flux solids, with or without free alkali. The balance of the composition comprises a volatile vehicle. Preferably there is the further limitation, namely that the total solids range by weight from approximately 10% to about 25% of the whole, while the total liquid content correspondingly ranges by weight from about 90% to about 75%.

A preferred composition, with a more limited range of ingredients, essentially consists of about 5 to 20 parts by weight of substance of the group inorganic oxides, silicates, chromates and molybdates, about 0.5 to 3 parts of total flux solids, with or without free alkali, about 4 to 15 parts organic resin solids, and the balance being a volatile vehicle in desired amount.

The organic resins which I employ are selected from the group of such polyacrylates, polyethylenes, polystyrenes, phenolics, alkyds, rosin derivatives and ester gum derivatives as are miscible with alcohol.

For the flux solids, I prefer to employ free chlorendic acid (hexachloroendomethylenetetrahydrophthalic acid, or more properly 1,4,5,6,7,7-hexachlorobicyclo-(2.2.1)-5-heptene-2,3-dicarboxylic acid) or derivatives thereof, these serving to promote sintering of the refractory during firing in order to obtain lower porosity, and to flux the early stage oxidation products on the metal surface to which the coating is applied in order to obtain a more intimate contact between coating and metal. Typical of the chlorendic acid derivatives which may be effectively employed are its alcoholates, esters, amines and other ammonia derivatives. The solvent action imparted by these derivatives is highly advantageous in that it contributes importantly to achieving a uniform coating on steel surfaces heretofore difficult of treatment, such as those which have been contaminated with traces of oil, drawing lubricants, rolling smut and the like. Additionally, these fluxes serve to facilitate, in controllable manner, bonding of the siliceous inorganic elements of the formulation to the surface of the metal products undergoing protection. And this is especially advantageous in those instances, as is frequently encountered in mill practice, where the surfaces undergoing treatment initially display a covering of mill (hot-roll) scale. I find that the protective effect thus imparted by my new formulation endures to such extent that upon removal of the protective coating at the conclusion of a high temperature treatment the surfaces of the metal are found to be substantially free of pitting.

Where desired, the chlorendic acid fluxing products may be supplemented with an additional common fluxing constituent such as borax, sodium carbonate, sodium silicate and the like. I find, however, that these additives are not essential to the successful practice of my invention. In this connection, care should be exercized not to include inorganic halogen-containing fluxes, of which silicofluorides, cryolites and fluorspar are typical. For these inorganic halogenates are observed to attack the surface of supposedly protected metal products, particularly the stainless steels.

As a substitute, either whole or in part, for the free chlorendic acid inclusion, I may employ any water-dispersible halogen-containing organic, reaction products of chlorendic acid with resinous materials, of which the Hetron resins of the Durez Plastics Division of Hooker Chemical Corporation are typical.

The coating formulation of my invention may be applied in desired suitable manner to the surface of the metal product to be protected as by dipping the metal product into a batch of the coating composition, by brush coating, or by spraying. The coating may be either air-dried and the coated product then charged into the furnace; or reliance may effectively be had upon the initial stages of the heat-treatment within the furnace to dry and set the coating on the metal surface. It is entirely feasible and practicable, where desired however, to include a drier in the coating composition.

I have found that the protective coating composition of my invention can be advantageously applied in desired simple and direct manner to a variety of stainless steel types and grades, typically including but not being limited to 17–4PH [1] (about 17% chromium, 4% nickel, 3% copper, and remainder iron), PH14–4Mo [1] (about 14%

[1] Trademarks Armco Steel Corporation.

chromium, 4% nickel, 3% molybdenum, 1% aluminum, and remainder iron), 17–7PH [1] (17% chromium, 7% nickel, 1% aluminum, and remainder iron), Type 303 (about 18% chromium, 9% nickel, .15% max. carbon, with 0.07% min. phosphorus, sulphur or selenium, and remainder iron), Type 302 (about 18% chromium, 9% nickel, and remainder iron), Type 410 (about 12% chromium, .15% max. carbon, and remainder iron), and Type 430 (about 16% chromium, .12% max. carbon, and remainder iron). Moreover, the protective coating is admirably imparted to a variety of metal surfaces, including those of centerless-ground, hot-rolled, cold-rolled, and cold-drawn products. Protection was observed to effectively endure at heat-treating temperatures ranging from 800° F. up to as high as 1950° F. or even more.

Removal of the protective coating, following completion of heat-treatment, may be accomplished in one or more of several different manners. Thus, reliance may be placed upon gentle sand-blasting, following removal of coated products from the furnace, although less vigorous removal techniques usually suffice. In many instances I find that much of the coating pops off simultaneously as the metal cools in the outside air, following removal from the furnace.

A number of typical formulations according to my presently preferred practice are listed in the following Table I, these formulations affording excellent protection to the surfaces of stainless steels of widely varying composition.

I find that Examples 3 and 8 of the following are perhaps to be preferred, as best combining low-cost both of materials and of production, with assurance of requisite protection to the surface of stainless steel grades of widely varying compositions.

In the following Table II, I disclose six other specific examples of formulations following the teaching of my invention. These I find to afford a somewhat greater protection to the metal surfaces than do the compositions according to Table I, at the same time displaying increased immunity to a wide variation of the atmosphere within the furnace.

TABLE II

Six examples of protective coating formulations having lower atmosphere sensitivity (Parts by weight)

Inorganic Ingredients	11	12	13	14	15	16
Colloidal Silica (Dav. Syloid-244)	3.7	2.6	2.4	2.6	2.4	2.1
Velva Clay (Min. Pig. C-163) [1]	3.6	------	1.7	1.3	2.4	1.1
Chrome Oxide (Min. Pig. 5310)	4.5	3.8	3.6	3.9	3.6	3.7
Barium Chromate (M.P. #1355)	------	3.8	3.8	3.8	3.6	4.3
Molybdate Orange (M.P. #2255)	------	1.4	------	1.4	------	1.1
Alumnia (Monsanto Chem., Micria-Al)	------	1.4	------	------	------	------
Strontium Chromate (M.P. #1365)	1.4	------	------	------	------	------
Lithium Carbonate (Technical)	------	0.7	------	------	0.7	0.2
Lithium Metasilicate (Technical)	------	------	1.4	------	------	------
Borax (Technical Grade)	0.4	------	------	0.4	------	0.4
Total Inorganic Solids	13.6	13.7	12.9	13.4	12.7	12.9
Vehicle Ingredients and Fluxes: Ammonium Polyacrylate (Solids)	2.0	2.0	2.0	2.0	2.0	2.0
Durez Resin 17211 (Solid) [2]	7.5	7.5	7.5	7.5	7.6	7.5
6% Mn-Octasol, Drier [3]	0.1	0.1	0.1	0.1	0.1	0.1
Wetting Agent (Tergitol-7)	0.1	0.1	0.1	0.2	0.1	0.1
Resin Solids and Additives	9.7	9.7	9.7	9.8	9.8	9.7
Flux (Chlorendic Acid)	0.6	0.6	0.4	0.6	0.4	0.6
Water (total)	31.9	31.8	32.2	31.8	32.1	32.2
Alcohol (Synasol, Reg.)	42.8	42.8	43.4	43.0	43.5	43.2
Ammonium Hydroxide (28%)	1.4	1.4	1.4	1.4	1.5	1.4
Volatile Vehicle	76.1	76.0	77.0	76.2	77.1	76.8
Total Vehicle Constituents (Resin Solids and Additives plus Flux plus Volatile Vehicle)	86.4	86.3	87.1	86.6	87.3	87.1
Totals (Inorganic Solids plus Vehicle Constituents)	100.0	100.0	100.0	100.0	100.0	100.0

TABLE I

Ten examples of protective coating formulations (parts by weight)

Inorganic ingredients	1	2	3	4	5	6	7	8	9	10
Colloidal Silica (Davison Chemical, Syloid-73)	5.0	4.5	8.7	9.4	------	------	------	------	------	------
Colloidal Silica (Davison Chemical, Syloid-244)	------	------	------	------	4.3	4.3	4.3	3.5	3.5	3.5
Alumina (Monsanto Chemical, Micria-Al)	------	------	2.8	------	------	------	------	------	------	------
Magnesium Oxide (Baker's Reag. Pow.)	------	------	0.9	------	------	------	------	------	------	------
Asbestos (Johns-Manville, No. 7RF1)	------	------	------	4.6	------	------	------	------	------	------
Kaolin (Baker's Tech. Powder)	5.0	4.5	------	------	------	------	------	------	------	------
Chromic Oxide (Amend Drug & Chem., C.P.)	------	4.0	5.8	------	------	------	------	------	------	------
Velva Clay (Mineral Pigments #C-163) [1]	------	------	------	------	4.5	4.5	4.5	3.6	3.6	3.6
Chrome Oxide Green (Min. Pig. No. 5310)	------	------	------	------	1.3	1.3	3.0	3.0	3.0	3.0
Iron Oxide Yellow (Syn-Min. Pig. #1112)	------	------	------	------	2.5	------	------	------	------	------
Iron Oxide Red (Nat.-Min. Pig. #3124)	------	------	------	------	------	2.5	------	------	------	------
Chromium Phosphate (Min. Pig. No. 5375)	------	------	------	------	------	------	0.8	------	------	------
Molybdate Orange (Min. Pig. No. 2255)	------	------	------	------	------	------	------	2.5	------	------
Barium Chromate (Min. Pig. No. 1355)	------	------	------	------	------	------	------	------	2.5	------
Strontium Chromate (Min. Pig. No. 1365)	------	------	------	------	------	------	------	------	------	2.5
Total Inorganic Solids	10.0	13.0	18.2	14.0	12.6	12.6	12.6	12.6	12.6	12.6
Vehicle ingredients and fluxes: Ammonium Polyacrylate (Resin solids from Acrysol-G-110, Rohm & Haas)	3.0	3.0	4.1	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Durez Resin 15546 (Durez Plastics Division)	------	2.8	------	5.7	------	------	------	------	------	------
Durez Resin 17211 (Durez Plast. Div.) [2]	------	------	------	------	7.4	7.4	7.4	7.4	7.4	7.4
Borax (Tech. Gr.)	0.2	0.2	------	------	0.4	0.4	0.4	0.4	0.4	0.4
Chlorendic Acid (Hooker Chemical)	0.4	0.2	0.6	0.5	0.3	0.3	0.3	0.3	0.3	0.3
Wetting Agent (Union Carbide, Tergitol-7)	0.8	0.7	------	0.5	0.3	0.3	0.3	0.3	0.3	0.3
Free Alkali (From 28% Aqueous Ammonia)	0.2	0.1	0.6	0.3	1.5	1.5	1.5	1.5	1.5	1.5
Metallic Drier (6% Mn-Octasol-Nuodex) [3]	------	------	------	------	0.1	0.1	0.1	0.1	0.1	0.1
Water (Total)	35.0	34.0	56.0	38.5	32.2	32.2	32.2	32.2	32.2	32.2
Alcohol (Carbide & Carbon's Synasol, Reg.)	50.4	46.0	20.5	38.5	43.2	43.2	43.2	43.2	43.2	43.2
Total vehicle constituents	90.0	87.0	81.8	86.0	87.4	87.4	87.4	87.4	87.4	87.4
Totals [3] (Inorganic Solids plus Vehicle Ingredients and Fluxes)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[1] Clay.
[2] Water-dispersible, rosin-maleic anhydride type polyester resin.
[3] Organometallic drier and/or metallic soap.

Finally, I provide six additional formulations in the following Table III providing a particularly high degree of protection to stainless steel surfaces at elevated temperatures.

TABLE III

Six examples of protective coating formulations with increased toughness and mar resistance (Parts by weight)

Inorganic Ingredients	17	18	19	20	21	22
Colloidal Silica (Dav. Syl. 244)	2.6	3.4	3.2	2.5	2.5	2.5
Velva Clay (Min. Pig. C-163)[1]	1.5	1.8	1.8	1.4	1.4	1.4
Chrome Oxide (Min. Pig. 5310)	4.0	4.9	4.7	3.7	3.7	3.6
Barium Chromate (M.P. #1355)	4.0	4.9	4.7	3.7	3.7	3.7
Molybdate Orange (M.P. #2255)	1.5	1.8	1.8	1.4	1.4	1.4
Borax (Technical Grade)	0.4	0.5	0.5	0.4	0.4	0.4
Total Inorganic Solids	14.0	17.3	16.7	13.1	13.1	13.0
Vehicle Ingredients and Fluxes:						
Durez Resin 17211 (Note 1)[2]	3.2			5.8	5.8	5.8
Durez Resin 19788 (Note 2)[2]		6.8	7.1			
Borden's Lemac 541-20 (Note 3)[4]	3.2	2.4	4.7			
Acrysol P-6N (Note 4)	3.2	3.1			3.7	
Acrysol Solution SR-1 (Note 5)[5]				3.7		
Monsanto Lytron 822 (Note 6)						3.7
Resin Solids	9.6	12.3	11.8	9.5	9.5	9.5
6% Mn-Octasol, Drier[3]	0.1	0.1	0.1	0.1	0.1	0.1
Wetting Agent, Tergitol-7	0.2	0.2	0.2	0.2	0.2	0.2
Chlorendic Acid	0.6	0.8	0.7	0.6	0.6	0.6
Fluxes	0.9	1.1	1.0	0.9	0.9	0.9
Ammonium Hydroxide (28%) Reagent	1.4	2.7	3.8	1.2	1.2	1.6
Water (Total)	48.1	33.8	33.6	40.3	40.3	40.0
Alcohol (Synasol, Regular)	26.0	32.8	33.1	35.0	35.0	35.0
Volatile Vehicle	75.5	69.3	70.5	76.5	76.5	76.6
Total Vehicle Constituents (Resin Solids plus Fluxes plus Volatile Vehicle)	86.0	82.7	83.3	86.9	86.9	87.0
Totals	100.0	100.0	100.0	100.0	100.0	100.0

[1] [2] [3] As in Table I.
[4] Water-dispersible and/or alkali soluble polyvinyl acetate resin.
[5] Water-dispersible carboxylated polyacrylate resin.

The formulations according to Table III particularly demonstrate high degree of toughness and as well, resistance to damage by mechanical handling. It is to be noted that these examples uniformly possess higher contents of inorganic solid, particularly of the more refractory ones, than do the first described formulations. From the embodiments of Table III, I find that Examples 17, 18 and 19 give superior results, and hence constitute preferred compositions.

As specifically illustrative of the practice of my invention I prepared a liquid protective coating by compounding 20 grams of colloidal silica with 20 grams of kalolin, 60 grams of ammonium polyacrylate solution (a 22% part of which comprised solids), along with ¾ of a gram of borax, 18 grams of chromic oxide, 100 ml. of 12% aqueous resin solution, 3 ml. of wetting agent, 2 ml. of 28% ammonia, ¾ gram of chlorendic acid and 100 ml. of alcohol. I ground these ingredients in a one-quart steel ball mill for approximately one hour. After thorough intermix, I added an additional 150 ml. of alcohol thinner. Grinding was continued for an additional 15 minutes, following which the mill was opened and about 350 ml. of compounded formulation thus provided was removed and placed in a suitable dipping container.

I dip-coated two test specimens with the formulation thus prepared. Following dip-coating, these specimens were dried for approximately 20 minutes at a temperature of approximately 180° F. A second dip coat was applied in the same manner, following which the specimens were dried for an additional 20 minutes at about 180° F. These

test specimens were of 17–4PH stainless steel, four inches in length, and ½ inch in diameter, with centerless-ground surfaces.

As part of the same series of tests, I prepared two additional specimens, these being hot-rolled and each approximating 4 inches in length and about ¾ inch round, and likewise of 17–4PH stainless steel. The surfaces of these additional specimens were characterized by a tightly adherent film of hot-roll scale and smut. Two dip coats of the protective coating were applied in technique duplicating that outlined above in connection with the two first described specimens.

All four specimens were thereupon placed in an electric furnace maintained at a temperature of 1900° F. For contrast, and as standards, I placed duplicate uncoated specimens of each surface condition in the furnace in order that they may be subjected to the same operating temperature conditions and for the same duration. At conclusion of exposure for one hour to furnace temperature of 1900° F., I removed one coated specimen of each surface type (centerless ground and hot-rolled) from the furnace and one corresponding uncoated specimen. I subjected the remaining two coated specimens and the uncoated specimens to total exposure of four hours duration at the temperature of 1900° F.

In both instances the surfaces of the uncoated specimens were found to be pock-marked, roughened and severely scaled following the high temperature exposure. Additionally, the uncoated four-hour specimens were found to be more severely damaged than the uncoated one-hour specimens. Moreover, all uncoated specimens were materially reduced in weight, and suffered appreciable loss in cross-sectional area.

In sharp contrast with the foregoing was the effective protection afforded the coated specimens. In no instance, that is, neither of the one-hour nor of the four-hour specimens, was appreciable change observed in either weight or cross-sectional area. These coated specimens exhibited smooth surfaces, free from pock marks, pits, or other undesirable blemishes. Noteworthy was the somewhat lustrous surface still exhibited by the two centerless-ground specimens upon removal of the protective film.

I found the protective film to remain firmly adherent throughout the entire heat-treatment, demonstrating no tendency towards peel, until cooling following termination of the high temperature treatment. And the film which did not spontaneously pop off during cooling was readily removable through gentle brushing, and this without need for pickling or other chemical or other special treatment.

As further illustrative of my invention, I subjected four specimens of cold-rolled sheet coupons to two dip coats of the protective composition described in the foregoing. These specimens each measured 1⅛ inches x 4½ inches x 0.025 inch thickness. Upon drying the protective coatings thereon, I subjected the specimens to heat-treatment at 1450° F. for 25 minutes, along with a single uncoated standard. Following removal of the specimens from the furnace and cooling and upon removal of the protective film, I found the coated specimens to be bright, lustrous and unblemished. Quite on the contrary, the uncoated standard specimen was spotted with brown-black scale, and was dull and tarnished in appearance.

Another specific example of typical practice according to my invention consisted of preparing three hot-rolled 17–4PH bars 1$\frac{9}{16}$ inches round by 14 feet in length. And following application of protective coating composition in manner hereinbefore disclosed, employing a formulation according to Example No. 2 (Table I), I solution-treated these bars at 1925° F. for three hours. The heat-treated bars, because of the quality of the surface, required much shorter pickling cycle than did an unprotected companion specimen.

Again, 16-foot hexagonal bar specimens of cold-drawn 17–4PH, with cross-sectional dimension of $\frac{25}{32}$ inch, were solution-treated at 1925° F. for three hours, having first

been provided with a protective coating according to Example 7 (Table I). The resultant product consistently demonstrated smoother surfaces than did the unprotected companion specimens.

Additionally, first protecting the metal with a protective coating according to Example 6 (Table I) and applying the same through dipping, I annealed 300 pound coils of 3/16 inch by 1 inch 18–8 (about 18% chromium, 8% nickel, and remainder iron) cold-rolled flats at 1900° F. for ¾ of an hour. The coated products displayed smoother surfaces and demonstrated markedly lower dimensional loss than did companion and unprotected test coils. The same advantageous results attended treatment of cold-rolled 18–8 flats and hot-rolled 18–8 FM (about 18% chromium, 8% nickel, 0.15% min. sulphur, and remainder iron) coils of ⅜ inch round.

To demonstrate that the coating composition could be effectively applied in manner other than dipping, I sprayed eight 14-foot hexagonal bars of cold-drawn 18–8 FM, measuring 21/32 inch in cross-sectional dimension, and employing for this purpose compositions similar to Examples 14 and 16 (Table II). The resulting products, in this test-treated manner generally hereinbefore described, exhibited lower dimensional loss and required shorter pickling cycles than did companion but unprotected materials.

It is apparent from the foregoing that my new formulation enjoys the many advantages set forth above. It is readily produced with low cost materials. And this, through readily available processing techniques. The formulation is applied for the thorough protection of metal surfaces with full assurance of retained surface quality. The method of treating and protecting stainless steel products is effective through a wide range of operating temperatures in a variety of furnace atmospheres. Such formulation responds to the requirement of resistance to damage by mechanical handling and of freedom from undesirable effects such as intergranular attack. Low toxicity is demonstrated, together with freedom from fire hazard.

My new process of treating steels, and as well, the new coating formulation which implements that process, afford adequate protection to the coated metal products through wide range of temperatures. This range may extend, for illustration, from about 800° F. up to 1950° F. or more. Moreover, such protection endures and is effective over long duration of treatment.

Both my new formulation and my new method of processing steel products have widespread application throughout the metal trades, embracing the steel mill and the fabricator as well, and this to a wide variety of steels, including not only the stainless steels, particularly the chrome-nickel grades and the hardenable grades of straight-chromium steels, but other steels as well, including those of both high and low alloy content, and the carbon steels. This protection extends to steels heretofore difficult in processing. Especially is this true of the stainless steels, where practically all forms and conditions of the metal products, whether wrought or cast or in converted form, are subjected to high temperature heat-treatment at some stage of processing. Such protection is particularly important with those grades of stainless steels where the chromium content is on the low side, as for example, 17–4PH, where tendency towards formation of scale ordinarily is quite severe.

My invention has effective application to steels in wrought form, such as hot-rolled, cold-rolled, drawn or forged products and steels in the form of castings. Various converted forms are advantageously processed according to my disclosure, illustratively including, but not being limited to, sheet, strip, bars, rods, and wire. And those highly polished metal surfaces heretofore quite difficult of protection respond admirably to my new process. For I find that my coating formulation, readily applicable to such polished surfaces, clings tenaciously, and this even in the green condition of the coating. While I do not desire to be bound by such explanation, quite possibly this advantageous phenomenon attends the range of particle size of the finely divided inorganic inclusions in the composition, perhaps coupled with the action of the wetting additive. Thus, bright, cold-drawn products are effectively protected. The protective qualities extend, as well, to hot-rolled products with attendant surface accumulation of tenaciously clinging mill scale ordinarily formed thereon.

Typical of the wide scope of the application of my invention is the processing of formed, finished and machined articles of, for example, the precipitation-hardenable grades of steel. I find that when, following such forming or machining to close surface detail and dimensional tolerances, these products are hardened by subsequent heat-treatment, this can be achieved without material loss of dimension or surface detail, when such products are preliminarily protected by application of my protection coating.

Both the process and the coating formulation demonstrate special advantage in the batch processing of products such as coils, rods, wire, and the like. When a large tonnage batch, say from 3 to 6 tons or more, is introduced into the furnace the temperature of the furnace is at once knocked down a substantial amount. There follows a transitory phase of furnace operation during the course of which normal operating temperature is gradually restored. Again, with such batch treatment, close control of the furnace atmosphere is virtually impossible. My new coating, however, is relatively insensitive to any of neutral reducing or oxidizing furnace atmospheres. This is an important practical advantage, for during initial restoration of the furnace to its operating temperature and at temperature, the subsequent heat-treatment, the products are adequately protected by my coating, whereas those metal products without the coating are observed to become pretty well oxidized, with formation of heavy scale on the untreated metal surfaces.

Substantially regardless of the product undergoing processing, then, the coating when once applied displays requisite adhesion while in its green form, with all required flexibility and toughness once it has set up in dried form, and with all requisite resistance to mechanical abrasion. After affording all required protection to the metal during heat-treatment it is nevertheless possible, upon conclusion thereof, and upon cooling the protected products following such heat-treatment, to readily remove this coating. For since a substantial part of the protective coating pops off spontaneously during cooling following termination of the heat-treatment, only limited pickling treatment, as in a dilute aqueous solution of nitric acid, is required to complete removal of the coating. Frequently, this pickling treatment is entirely eliminated, as in those instances where it is demonstrated that such scale as does not pop off spontaneously is directly removed by simple brushing under water. I find my new composition to serve as a diffusion barrier on the metal, so that the alloy components of the steel are not subjected to either oxidation or reduction. The formulation itself is relatively inert as concerns the underlying surface of the metal. Thus, intergranular penetration is minimized. The same is true of attack upon or damage of the surface of the metal by the constituents of the coating formulation.

All the foregoing, as well as many other highly practical advantages, attend the practice of my invention.

It is apparent from the foregoing that once the broad aspects of my invention are disclosed, many embodiments thereof will suggest themselves readily to those skilled in the art, all falling within the scope and spirit of my invention. Accordingly, I desire the foregoing disclosure to be considered as simply illustrative, and not as imposing limitations.

I claim as my invention:

1. The method of preparing metal stock for protection against surface attack during high-temperature treatment, which method comprises providing a colloidal formulation consisting essentially of 3 to 45 parts by weight of substance selected from the group consisting of inorganic oxides, silicates of aluminum and magnesium, chromates and molybdates, 1 to 40 parts organic resin, and .2 to 10 parts of water-dispersible halogen-containing organic flux, all in an aqueous-alcohol solution; coating such formulation upon the surface to be treated; and thereupon drying the coated formulation in closely bonding protective sheath upon the metal surface.

2. The method of heat-treating alloy steel products comprising first coating the surfaces of the products with a composition consisting essentially of finely divided silica admixed with refractory inorganic substances selected from the group consisting of oxides, silicates of aluminum and magnesium, chromates and molybdates, together with an organic resinous binder along with a chlorendic acid flux, all uniformly dispersed in stable suspension in an aqueous-alcohol solution; drying the coating as thus applied; subjecting the coated steel products to required high temperature heat-treatment; and thereupon cooling the metal products and removing such retained coating as has not spontaneously popped off during cooling.

3. The method of heat-treating alloy steel products comprising first coating the surfaces of the products with a composition consisting essentially of finely divided silica admixed with refractory inorganic substances selected from the group consisting of oxides, silicates of aluminum and magnesium, chromates and molybdates, together with an inorganic resinous binder along with water-dispersible halogen-containing organic flux, all uniformly dispersed in stable suspension in an aqueous-alcohol solution, in which composition the total solid content thereof ranges from about 20% to 47½% by weight and the total liquid content ranges from about 53½% to 80%; drying the coating as thus applied; subjecting the coated steel products to required high temperature heat-treatment at about 900° F. to 2000° F.; and thereupon cooling the metal products and removing such retained coating as has not spontaneously popped off during cooling.

4. A coating composition for application to the surfaces of metal for the protection thereof in subsequent heat-treatment, said composition consisting essentially of solid ingredients and volatile vehicle, the solid ingredients consisting essentially of: about 3 to 45 parts by weight of substance selected from the group consisting of inorganic oxides, silicates of aluminum and magnesium, chromates and molybdates; about 1 to 40 parts organic resin; and about .2 to 10 parts water-dispersible halogen-containing organic flux capable of effecting sintering of the inorganic constituent and promoting intimate contact between coating and metal.

5. A coating composition for application to the surface of metal for the protection thereof in heat-treatment, with subsequent ease of removal, said composition consisting essentially of solid ingredients and volatile vehicle, the solid ingredients consisting essentially of: 3 to 45 parts by weight of substance selected from the group consisting of inorganic oxides of silicon, aluminum, magnesium, iron, molybdenum, titanium, nickel, chromium and zirconium, silicates of aluminum and magnesium, chromates of barium, lead and strontium and molybdates; 1 to 40 parts organic resin; and .2 to 10 parts flux selected from the group consisting of chlorendic acid alone and chlorendic acid with a free alkali capable of effecting sintering of the inorganic constituent and promoting intimate contact between coating and metal.

6. A coating formulation for protecting steels during high temperature treatment, with subsequent ease of removal, consisting essentially of: 3 to 45 parts by weight of inorganic substance consisting essentially of finely divided silicon dioxide, together with an admixture of at least one powdered refractory substance selected from the group consisting of the refractory grades of oxides, silicates of aluminum and magnesium, chromates and molybdates; 1 to 40 parts of water-dispersible organic resinous binder; .2 to 10 parts flux selected from the group consisting of free chlorendic acid and its derivatives; and remainder aqueous-alcohol solvent, the said solvent amounting to about 75% to 90% by weight of the formulation.

7. A coating formulation for protecting stainless steel surfaces during high temperature heat-treatment, with subsequent ease of removal, consisting essentially of: 3 to 45 parts by weight of inorganic solids consisting of finely divided silicon dioxide together with at least one powdered substance selected from the group consisting of alumina, hydrated aluminum silicate, magnesia, hydrated magnesia silicate, chromium oxide, nickel oxide, titanium oxide, zirconia, barium chromate, lead molybdate, lead chromate, and strontium chromate; 1 to 40 parts of water-dispersible organic resinous binder selected from the group consisting of such polyacrylates, polyethylenes, polystyrenes, phenolics, alkyds, resin derivatives, and ester gum derivatives as are miscible with alcohol; .2 to 10 parts flux selected from the group consisting of free chlorendic acid and its derivatives; and remainder an aqueous-alcohol solvent.

8. A compound for the protection of the surface of stainless steel during high temperature heat-treatment, with subsequent ease of removal, consisting essentially of: 3 to 45 parts by weight inorganic solids consisting essentially of silica, kaolin, polyacrylate solution, borax and chromic oxide; 1 to 40 parts water-dispersible organic resinous binder; and .2 to 10 parts flux consisting of aqueous resin solution, aqueous ammonia, and chlorendic acid, said inorganic solids, resinous binder and flux intimately admixed and colloidally suspended in an aqueous-alcohol solution.

9. A coating formulation for protecting the surface of metal during heat-treatment, with subsequent ease of removal, consisting essentially of solid ingredients and volatile vehicle, the solid ingredients consisting essentially of: ingredients selected from the group consisting of inorganic oxides of silicon, aluminum, magnesium, iron, molybdenum, titanium, nickel, chromium and zirconium, silicates of aluminum and magnesium, chromates of barium, lead and strontium and molybdates, at least one of which is refractory in character, ranging from about 3% to about 45% by weight of the solid constituents; organic resin solids ranging from about 1% to about 40% of the solids; and water-dispersible halogen-containing organic flux solids and free alkali ranging from about 0.2% to about 10% of the solids, the said solid ingredients being carried into uniform and stable suspension in said volatile vehicle, with the further limitation that the said solids range from about 12.5% to about 17.5% by weight of the whole, while the said liquid ranges from about 87.5% to about 82.5%.

10. A coating formulation for protectiing steel products during high temperature heat-treatment, with subsequent ease of removal, consisting essentially of: colloidal silica from 3.5% to 8.7% by weight of the whole; alumina up to 2.8%; magnesium oxide up to 0.9%; chromic oxide up to 5.8%; chrome oxide green up to 3.0%; clay up to 3.6%; molybdate orange up to 2.5%; ammonium polyacrylate 2.0% to 4.1%; other resin solids up to 7.4%; borax up to 0.4%; chlorendic acid from 0.3% to 0.6%; metallic drier up to 0.1%; a wetting agent up to 0.3%; free alkali from 0.6% to 1.5%; water from 32.2% to 56.0%; and alcohol from about 20.5% to about 43.2%.

11. A protective coating composition for the surfaces of stainless steel and generally similar products during high temperature heat-treatment, with ease of removal

subsequent to such treatment, consisting essentially by weight of approximately: colloidal silica 2.6% to 3.2%; clay 1.5% to 1.8%; chrome oxide 4.0% to 4.7%; barium chromate 4.0% to 4.7%; molybdate orange 1.5% to 1.8%; borax 0.4% to 0.5%; rosin-maleic anhydride polyester resin 3.2% to 7.1%; polyvinyl acetate resin 3.2% to 4.7%; carboxylated polyacrylate resin up to 3.2%; drier 0.1%; 0.2% wetting agent; chlorendic acid 0.6% to 0.7%; ammonium hydroxide (28% solution) 1.4% to 3.8%; water 33.6% to 48.1%; and alcohol 26.0% to 33.1%.

12. Stainless steel having thereon a flexible, tough and abrasion-resisting coating protecting the surface thereof against scaling in heat-treatment, with ease of removal subsequent to such treatment; which coating initially consists of solid ingredients and liquid vehicle, the said solid ingredients consisting essentially of: about 3 to 45 parts by weight of inorganic substance selected from the group consisting of inorganic oxides, silicates of aluminum and magnesium, chromates and molybdates; 1 to 40 parts of organic resin; and .2 to 10 parts flux selected from the group consisting of chlorendic acid alone and chlorendic acid together with a free alkali capable of effecting sintering of the inorganic constituents and promoting intimate contact between coating and metal surface, all suspended in said liquid vehicle.

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