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PROCESS FOR COATING AND HEAT TREATING A
METAL ARTICLE AND COATING COMPOSITION
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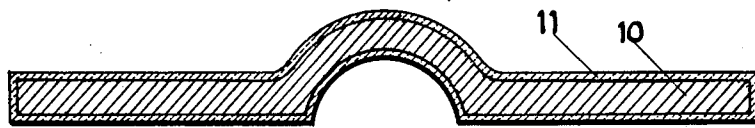


Fig. 1

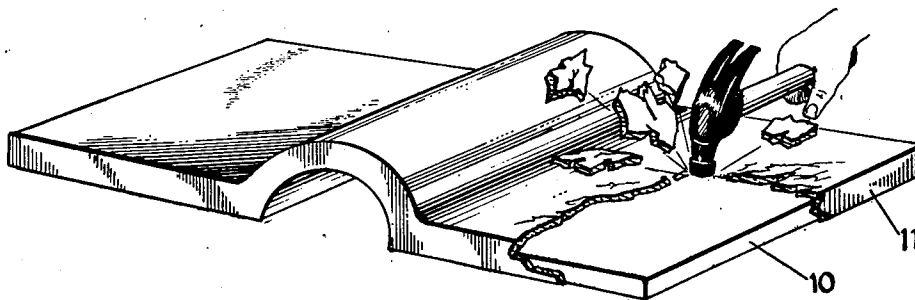


Fig. 2

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PROCESS FOR COATING AND HEAT TREATING A METAL ARTICLE AND COATING COMPOSITION

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This invention relates to a novel composition applied to metal-containing objects such as castings to protect such objects against metal oxidation or other surface reactions during heat treating. More particularly, this invention relates to a composition which will form a glaze about the object, the glaze being impermeable by oxygen and easily removed after heat treatment.

Such metal-containing objects will hereinafter be referred to as castings. The teachings of this invention may, however, be applied to metal-containing objects, shapes and forms no matter how made. Many types of metal castings, especially those of steel or alloy steels, are heat-treated to impart desired physical properties to them. Heat-treating normally consists of heating the casting to as high a temperature as 2150° F. for an extended period of time. At the temperatures used, the surface of the casting readily reacts with atmospheric gases, particularly with oxygen to form a coating of the metal oxide on the casting. This coating may be removed chemically, or may be sandblasted off, either process being expensive both with regard to the loss of the metal and to the labor required. Because a portion of the casting surface must be removed, allowance must be made for this loss, and pattern sizes must be calculated to compensate for such losses.

One method used to provide an oxygen-free surface is to carry out the heat-treating process in an inert atmosphere. This method is however expensive, requiring specially designed furnaces and auxiliary equipment. It would, therefore, be desirable to have a type of protective coating which could be easily deposited on a metal casting before it is heat-treated and which could likewise be easily removed after heat-treating. The coating should not decarburize the casting surface, or become an integral part thereof; it should melt and flow about the casting (at temperatures about 1000° F.) without creeping or crawling and should not allow penetration of oxygen. Finally, the coating should be easily removed after cooling, preferably snapping off or cracking off like glass.

It is therefore a primary object of this invention to furnish a coating material suitable for protecting metal castings from being oxidized during heat-treating. Among other important objects of this invention may be listed

(1) To provide a method of protecting castings during heat-treating such that little or no metal will be lost to oxide formation or to removal by chemical or by physical means;

(2) To provide a coating material for castings which permits the castings to be heat-treated in an oxidizing atmosphere without becoming oxidized on the surface;

(3) To provide a protective coating which is easily put on castings, which does not need to be dried before exposing the casting to heat, and which may be easily removed after heat-treating;

(4) To provide a protective coating which may be put on castings without having to specially clean the castings before deposition of the coating;

(5) To provide a coating which affords protection at

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temperatures as low as about 1000° F. and which does not creep or crawl to permit gas penetration into the casting surface;

(6) To provide a protective coating for castings which does not decarburize the casting surfaces or become an integral part thereof;

(7) To provide a means of retaining and preserving the fine initial microfinish of castings molded by specialty and/or precision methods such as shell, lost wax, Mercast, Ceramicast and the like; and

(8) To provide a means of protecting the surfaces of metal-containing objects from corroding atmospheres irrespective of how the object was originally made, for example by casting, forging, machining, stamping, extruding, pressing and the like.

These and other objects will become apparent in the following detailed description of this invention.

The protective coating of this invention is a liquid suspension of compounds of aluminum, silicon, and one or more alkali metals, which in the process of heat-treating fuses to form a combination of crystalline and amorphous glassy phases of the oxides of aluminum, silicon and an alkali metal. These phases in turn form a thin, gas-imperious protective glaze over the casting. A small quantity of one or more of the oxides of nickel, cobalt and manganese may be present in the glaze to impart some bonding between the coating material and the surface of the casting. If desired, these compounds of nickel, cobalt and manganese may be added as oxides, as salts which are heat-convertible to oxides or as constituents of a relatively high fusion enamel frit.

The coatings for castings of this invention will be described in detail below, and with reference to the accompanying drawings in which:

FIG. 1 is a cross-sectional view of a casting having been covered with a coating of this invention before heat-treating; and

FIG. 2 is a perspective view of a casting in the process of having the coating removed after heat-treating.

Each of the three oxides, i.e., oxides of aluminum, silicon, and an alkali metal, must be present in the protective coating of this invention if it is to possess the desirable properties listed above. This is pointed up by the fact that ordinary refractory materials will not offer satisfactory protection because they permit oxygen penetration, and by the fact that high-temperature fusing enamels alone will not work because they become too tightly bonded to the casting surface for satisfactory removal after heat-treating. Moreover such enamels often sublime under the conditions required for heat-treating. Enamel coatings alone are therefore not satisfactory.

These oxides of aluminum, silicon and an alkali metal, in fusing, form several crystalline phases. X-ray spectra have been employed to identify such crystalline phases as quartz, tridymite, albite, and possibly mullite and nephelite. For convenience, the coating of this invention will be considered to be a mixture of the individual oxides of aluminum, silicon and an alkali metal, even though it is realized that the coating is actually composed of complexes of these various oxides. The composition of the final glaze may therefore best be described in terms of the total amounts of Al_2O_3 , SiO_2 and Na_2O (or other alkali metal oxide) required in the final glaze regardless of in what complex they are present.

It has been found that the three oxides should be present in certain specified ranges. Thus, the oxide of silicon, SiO_2 , should be present in a range from about 29 to 60% of the total weight of the coating composition; while aluminum oxide, Al_2O_3 , should be present in a

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weight range of from about 7 to 16%; and the oxide of the alkali metal, such as Na_2O , should be present in a weight range of from about 3 to 7.5%. Other alkali metals, e.g., potassium and lithium may be substituted for sodium. The remaining weight percent, i.e., from about 23 to 57% is the liquid material in which the oxides are suspended. Normally, this liquid will be water.

As an example, the nominal or average percent may be cited, i.e., 45% SiO_2 , 11% Al_2O_3 , and 5% Na_2O with 39% water. If these are recalculated on a dry basis, they become 74% SiO_2 , 18% Al_2O_3 , and 8% Na_2O . However, this is merely cited as an example and is not meant to be limiting in any way. The above percentages are not, however, intended to exclude small amounts of other reactable oxides which may be included for various purposes, nor does it include the amount of oxides of nickel, cobalt or manganese which may be introduced either as individual components or by the incorporation of minor amounts of them in high-fusing enamel frits.

The required oxides of this invention may be supplied in several different forms. Thus, the SiO_2 may be supplied in the form of aluminum silicate such as occurs in a high-fusion-point slip clay. A finely divided silica flour may also be used as a source of the SiO_2 along with some alkali silicates. It is also possible to replace some of the slip clay with fine sand or uncalcined fire clay.

The aluminum oxide is preferably supplied in the form of aluminum silicate from the slip clay. It may, however, be supplied to a minor extent from feldspar and from the uncalcined fire clay. The oxide of the alkali metal, such as sodium, potassium or lithium, is preferably supplied from sodium silicates, a small amount from feldspar, and if desired, from a carbonate such as sodium or potassium carbonate. Of the sodium silicates, the meta silicate, Na_2SiO_3 , is preferred.

Although these components may be used in various combinations to provide the required ranges for the three oxides, it has been found preferable to always use some slip clay, some sodium silicate and some silica flour. Compositions made up of only these three components along with water have been found to possess excellent protective properties but relatively short bath lives, i.e., they cannot be stored for an extended period of time. For this reason, additional components such as indicated are desirable. It may be noted that the higher the percent of the sodium silicate the more chance there is for coagulation to occur and hence the shorter the bath life.

As noted above, a small amount of enamel frit (up to about 3-11% of the total weight of the liquid coating) may be added to improve the adhering quality of the coating, or alternatively we may add small amounts of the oxides of cobalt, nickel, or manganese which are normally present in such frit materials. In place of the oxides of these metals, compounds which are converted to their respective oxides when heated may be used. It is believed that these oxides contribute to the adhering power of the coating material. When the oxides of cobalt, nickel, and manganese are added, it is preferable to add less than about 1%, total. This amount gives a marked improvement in adhering qualities.

When enamel frit is added, it should contain a substantial portion (50% or more) of high-fusion frit material, have a fusion point between 1600 and 1700° F. and an effective quantity (i.e., preferably from a few tenths of a percent to about 2% by weight) of one or more of the oxides of nickel, cobalt or manganese.

The liquid in which the oxides are dispersed is preferably water for economic reasons. However, any polar liquid which is a solvent for the sodium silicate may be used. A combination of water and another polar liquid is also feasible, the sodium silicate being dissolved first in the water. Thus, a coating containing half water and half glycerine as the dispersing or suspending medium for the oxides produces a good protective coating about the casting.

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The components of the coating of this invention are mixed in the dispersing medium to form a coating liquid which is easily deposited on the casting. It has been found preferable to dissolve the sodium silicate in water and then to add the other components to give a homogeneous dispersion of colloidal particles in the silicate solution. Additional water or other polar liquids may be added to give the desired consistency, usually similar to that of house paint.

The final liquid coating shows no tendency to settle out and the liquid may be stored for extended periods of time provided that it is not made up of only the slip clay, sodium metasilicate, and silica flour as noted above. When the percentage of sodium metasilicate is as high as it must be in this three-component system to provide the desired range of oxides, it tends to gel after several hours, probably forming silica gel which will then set up and harden.

In this method of mixing it is believed that the sodium metasilicate serves to keep all of the other components in suspension. The clay, in finely divided form, probably helps to support the other materials in the sodium silicate gel or suspension thus formed.

Objects are easily and uniformly coated with the liquid coating material of this invention by spraying, painting, dipping, or other suitable means. The coating once deposited on the casting surface will not run and it dries uniformly without cracking. The minimum thickness of coating ranges from about $\frac{1}{64}$ to $\frac{1}{32}$ of an inch. Coatings of this thickness will offer complete protection to the casting. However, when the coating liquid is further diluted with water to produce thinner coatings, they will not adhere to the casting. The maximum thickness is determined by economic considerations, anything over the minimum noted being suitable.

The coated casting may be placed in the heat-treating furnace before the coating has been completely dried. If the casting is placed in a heat-treating furnace not up to temperature and then brought up to temperature, the coating need be only partially dried. Thus, air drying of the coated casting before heat-treating is not necessary, although there is more of a tendency for the coating to blister when heat-treating is begun before the coating is dried. This blistering effect, however, has no apparent detrimental effect on the protection offered by the coating.

A typical casting is shown in FIG. 1. The casting 10 has been coated with the protective coating 11 of this invention. After heat-treating, the coating has a glaze-like character or is similar to glass in nature. FIG. 2 illustrates one means by which the coating may be removed, i.e., by hitting it lightly with a hammer. Alternately, the glaze may be removed by means of a wire brush, or any other convenient means. Since the coating is not effectively bonded to the casting surface, removal is a matter of cracking the glaze off rather than of using the ordinary harsher treatments such as wheel abrading or sandblasting. However, light sandblasting may be desirable to remove the glaze from parts of the casting which are otherwise difficultly accessible to such means as a wire brush or light tapping by a hammer for example.

The coating of this invention is applicable to all ferrous alloys and metal alloys containing iron, to titanium and titanium alloys, to mixtures such as cermets which contain metals and their alloys, or to other metallic alloys which upon heat application are subject to oxidation, decarburization, or other natural or unnatural atmospheric reactions. The metals, alloys, or mixtures may be produced by any of the forming techniques such as casting, forging, machining, stamping, extruding, powdered metal forming, etc.

Typical coating compositions are shown below in Table I.

TABLE I

Typical Compositions of Coating Material (in Percent
by Weight of Total Material)

Component	Composition									
	A	B	C	D	E	F	G	H	I	J
Slip Clay-----	10.8	15.8	27.1	14.0	21.0	21.0	11.8	11.9	17.8	13.8
Sodium Silicate-----	6.8	8.0	17.0	17.6	13.2	13.2	14.6	7.5	11.1	8.6
Silica Flour-----	10.8	15.8	27.1	28.0	21.0	21.0	11.8	23.9	17.8	13.8
Sand (100-mesh)-----	10.8	12.8	-----	-----	10.5	10.5	11.8	-----	17.8	13.8
Feldspar-----	29.8	13.9	-----	14.0	-----	-----	11.8	11.9	-----	8.6
Uncalcined Fire Clay-----	-----	-----	-----	-----	10.5	5.4	11.8	14.9	4.4	3.4
Sodium Carbonate-----	-----	0.4	-----	-----	-----	-----	-----	-----	-----	-----
Enamel Frit-----	-----	0.2	-----	-----	-----	-----	-----	-----	-----	-----
Cobalt Oxide-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Nickel Oxide-----	31	33.1	28.8	26.4	23.8	28.9	26.4	29.9	31.1	38.0
Water-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

These compositions were made up by dissolving the sodium silicate in about one-half of the water, which could be heated to accelerate the dissolving process, and then adding the solid ingredients in the following order: enamel frit or oxides of nickel, cobalt and/or manganese, feldspar, silica flour, uncalcined fire clay, any other ingredient or ingredients, and the remaining water as needed.

All of the above compositions except C exhibited good bath life, i.e., they could be made up and stored over an extended period of time. Composition C had a somewhat limited bath life, in the range of about two to eight hours. This composition did, however, give excellent protection to heat-treated objects.

Each of these compositions was deposited upon various types and shapes of castings and it was found that they gave good protection to the castings up to temperatures of about 2200° F. The results, in terms of weight losses suffered by heat-treated objects coated with two different examples of the composition of this invention are given below in Table II.

TABLE II

Weight Loss of Protected Metal Sample After Heat-Treating

Composition ¹	Wt. Before Coating (gm.)	Wt. After Cleaning (gm.)	Wt. Loss (gm.)	Wt. Loss of Blank Control (gm.)	Percent Wt. Loss Based on Blank	Remarks
C-----	147.6	147.1	0.5	9.5	5.3	Complete snap-off after cooling.
C-----	154.3	153.7	0.6	9.5	6.3	Complete snap-off with hammer blow.
C-----	157.1	156.6	0.5	8.9	5.6	Almost total snap-off left clean base metal.
F-----	152.1	152.0	0.1	6.6	1.5	Total snap-off.

¹ See Table I.

In obtaining the above data, small sample blocks of a low carbon low alloy steel were coated with the compositions noted, the coating was permitted to at least partially dry and the sample put in an oven for a 14-hour cycle, during 10 hours of which it was brought up to and maintained at 1700° F. From these data it will be seen that the loss to heat-treating when an object is coated with the composition of this invention is only a minor fraction of the loss suffered by an uncoated object.

Each of compositions A and B (see Table I) were applied to three different test samples of a low carbon low alloy steel designated AXS having the following nominal analysis: 0.30 C, 0.42 Si, 0.80 Mn, 0.60 Ni, 0.48 Mo, 0.05 (max.) K, 0.05 (max.) S, and 0.025 V. The six samples (three covered with composition A, three with composition B) were placed in a furnace at 1800° F. The temperature of the furnace was hourly raised by 100° F. and after three hours (that is after they had remained at 2000° F. for one hour) one of each of the sets was removed. Likewise one each of the sets was re-

moved after having been maintained at 2100° F. for one hour and at 2200° F. for one hour. The results of these runs are given below in Table III.

TABLE III

Composition ¹	Max. Temp. Before Removal, ° F.	Wt. Before Coating (gm.)	Wt. After Cleaning (gm.)	Wt. Loss (gm.)	Percent Wt. loss to Heat-Treating (gm.)	Percent Wt. loss to Heat-Treating of Blank Control
A-----	2,000	148.7	143.9	4.8	3.23	5.55
	2,100	154.8	148.2	6.6	4.26	6.62
	2,200	160.6	-----	-----	2.6	9.30
B-----	2,000	146.5	142.6	3.9	2.66	5.55
	2,100	140.7	-----	-----	2.35	6.62
	2,200	143.7	137.6	6.1	4.24	9.30

¹ See Table I.

² Estimated from plot.

These data not only indicate that the coating of this invention offers protection to objects exposed to atmospheres of 2000-2200° F., but they also illustrate the ad-

vantage of adding small amounts of the oxides of nickel and cobalt in composition B.

Tests based upon visual observation of objects which contained raised designs and numbers on their surfaces were also made. For example, test samples having raised numbers were covered with the coating composition of this invention and were heat treated. The glaze was removed after the test samples cooled and the numbers were found to be essentially as distinct as before heat treating. In contrast to this, when similar samples were heat treated without the protective coating the numbers were burned off. Moreover, the coating composition of this invention permits an object to retain a precision surface during heat treating.

It may be seen that by the practice of this invention it is possible to materially reduce, and even eliminate, the corrosion losses suffered by a metal-containing object during heat-treating by controlling or eliminating the two primary factors contributing to such corrosion losses, i.e., loss of weight and loss of surface detail.

In addition to protecting the casting from surface oxidation, the coatings of this invention materially reduce decarburization of the castings. In the case of low-carbon steels this is very important for no appreciable amount of carbon which is on the surface should be removed. When uncoated castings are heat-treated, decarburization has been found to penetrate to a depth of 0.025 inch while in castings protected by the coating of this invention, decarburization was found to a depth of only 0.002 inch.

The coating of this invention thus offers a simple inexpensive way of protecting casting surfaces during the heat-treating process. The coating material is easily applied and easily removed. Moreover with the degree of protection against surface oxidation attained, castings may be made directly to desired shape and size without allowance for surface oxide loss.

We claim:

1. A novel composition suitable for deposition on a metal-containing object to protect said object from corrosive atmospheres at temperatures up to about 2200° F., consisting essentially of compounds of silicon, aluminum and an alkali metal suspended in a liquid dispersing medium removable by vaporization, said compounds being heat-convertible to their respective oxides and being present in amounts such that the weights of their oxides are equal to about 29 to 60%, 7 to 16%, and 3 to 7.5% respectively, of the total weight of the composition.

2. A novel composition in accordance with claim 1 wherein said compounds of silicon, aluminum, and an alkali metal are present in the form of aluminum silicate, sodium silicates, and silica flour.

3. A novel composition in accordance with claim 1 wherein said liquid dispersing medium is water present in a weight range of from about 23 to 57% of the total composition.

4. A novel composition suitable for deposition on a metal-containing object to protect said object from corrosive atmospheres at temperatures up to about 2200° F., consisting essentially of a liquid dispersing medium removable by vaporization having suspended therein compounds of silicon, aluminum, and an alkali metal, and not more than about 1% by weight of at least one oxide of a metal selected from the group consisting of nickel, cobalt, and manganese; said compounds of silicon, aluminum, and an alkali metal being heat-convertible to their respective oxides and being present in amounts such that the weights of their oxides are equal to about 29 to 60%, 7 to 16%, and 3 to 7.5% respectively, of the total weight of the composition.

5. A novel composition in accordance with claim 4 wherein said oxide selected from the group consisting of

nickel, cobalt and manganese, is introduced in the form of a high-fusion enamel frit.

6. A novel composition in accordance with claim 4 wherein at least 50% of said dispersing medium is a polar liquid which is a solvent for sodium silicate.

7. A novel composition in accordance with claim 4 wherein more than one-half of said compounds of silicon, aluminum, and an alkali metal are present in the coating composition as slip clay, sodium meta silicate, silica flour, feldspar, and uncalcined fire clay.

8. Process for heat-treating an article at elevated temperatures to alter its properties, at least a surface thereof containing metal normally corrodible by heat-treating, characterized by the step of coating said surface prior to said heat-treating with a liquid coating composition applied to a thickness of at least $\frac{1}{64}$ of an inch, said coating composition consisting essentially of compounds of silicon, aluminum, and an alkali metal suspended in a liquid dispersing medium removable by vaporization, said compounds being heat-convertible to their respective oxides and being present in amounts such that the weights of their oxides are equal to about 29 to 60%, 7 to 16%, and 3 to 7.5%, respectively, of the total weight of the composition.

9. Process for heat-treating an article at least a surface thereof containing metal normally corrodible by heat-treating, comprising the steps of coating said surface with a liquid coating composition applied to a thickness of at least $\frac{1}{64}$ of an inch, exposing the resulting coated surface to heat-treatment at elevated temperatures thereby to alter the properties of said metal, cooling said heat-treated surface, and removing therefrom the resulting glaze formed by said coating during said heat treatment, said coating composition consisting essentially of compounds of silicon, aluminum and an alkali metal suspended in a liquid dispersing medium removable during said heat treating, said compounds being heat-convertible to their respective oxides and being present in amounts such that the weights of their oxides are equal to about 29 to 60%, 7 to 16%, and 3 to 7.5%, respectively, of the total weight of the composition.

10. Process in accordance with claim 9 further characterized by the step of introducing said surface to said heat-treatment before said coating is dry.

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