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CERAMIC COATING FOR METALS

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2 Claims. (Cl. 117-129)

1

This invention relates to a ceramic coating for iron, steel, and alloy metals, which will protect the metal thus coated from corrosion for long periods of time at elevated temperatures and will withstand severe mechanical shocks and impacts with a minimum of flaking and chipping. The coating is also extremely resistant to thermal shocks produced by rapid heating and cooling. This type of coating is particularly useful for covering and protecting the metal used in the exhaust disposal systems of internal combustion engines where the exhaust conduits and related parts are subjected to high temperatures, corrosive gases, mechanical shocks and strains, and thermal shocks caused by rain, snow, and sleet falling upon the system and by the heating and cooling of the system every time the engine is started and stopped.

So far as is known there were no ceramic coatings for metals which would effectively protect the metal from oxidation at high temperatures prior to the present invention. While a number of commercial "one coat" enamels intended for high temperature metal protection were extensively tested at 500° F., it was soon discovered that none of them would withstand heating at this temperature for any appreciable length of time. In most cases the start of oxidation was apparent after one hour of testing. In the case of the coating constituting the present invention, however, the high temperatures produced by hot exhaust gases may be applied to the coated metal for many hours without any serious consequences either to the metal or to the coating. In addition, the present coating will successfully withstand many cycles of thermal shock, such as that produced by heating the coated metal part to a high temperature and then plunging it into cold water immediately upon its removal from the furnace. Due to its excellent adherence to the metal, the coating has the capability of withstanding severe impacts or mechanical strains without undue cracking or flaking.

The coating to be hereinafter explained and described in detail is capable of producing these results by virtue of the composition and characteristics of the various ingredients going to make up the final coating. One of these ingredients, namely, first grade diaspore, is of particular value in this coating because of at least two important characteristics of this material. One of these characteristics is the hardness or refractoriness of this mineral and the other is the reluctance with which it goes into solution with the frit at high temperatures, together with the fact that the portion of the diaspore which

2

does go into solution with the frit does not appreciably alter its coefficient of expansion. This is of considerable importance where good adherence to the metal must be maintained over long periods of time since otherwise the coefficient of expansion will depart more and more from the designed value as time goes on until finally the coating will "pop" off of the metal by reason of the comparatively large disparity between the coefficient of expansion of the coating and the coefficient of expansion of the metal.

Accordingly, it is one of the objects of the present invention to provide a ceramic coating for ferrous or non-ferrous metals which will protect the metal for a considerable length of time from temperatures in the neighborhood of 1500° F., and also from the hot, corrosive gases of the type found in internal combustion engine exhaust systems.

It is another object of the present invention to provide a ceramic coating for metals which will successfully withstand numerous cycles of thermal shock without spalling, chipping, or cracking.

It is a further object of the invention to provide a ceramic coating for metals which will adhere well to the metal and will resist chipping and flaking when the metal is subjected to mechanical strains or blows.

It is a further object of the invention to provide a "one coat" ceramic composition having the above-mentioned qualities and which will serve as a foundation for subsequent coatings.

The coating composition comprising the present invention consists of a rather hard and refractory frit which has been found to be ideally suited for the purpose intended. This frit contains a large percentage of refractory materials, such as quartz and feldspar, a number of fluxing agents, such as borax, soda ash, soda niter, and fluorspar, and several metallic oxides for promoting the adherence of the coating to the metal. Metal compounds which at high temperatures decompose to oxides are of course equivalent of oxides. In order to provide the coating with the desired property of being able to protect the metal at high temperatures, for long periods of time, and to withstand numerous cycles of thermal shock, a considerable quantity of a highly refractory material is added as a mill addition. This material, namely, diaspore, has the added advantage of acting as a flotative agent in the slip, thereby eliminating the need of adding clay to the mill batch for this purpose.

The novel coating which we have discovered may be made to "fit" practically any type of

3

metal by adjusting the percentage of the soda ash which has a very high coefficient of expansion. Thus, for metals having a relatively low coefficient of expansion, a smaller amount of soda ash is used in the frit than for metals having a relatively high coefficient of expansion. In order to more clearly explain our discovery, the composition of two representative frits will be set out herein, the first of which, designated as frit "A" has been found to "fit" such metals as #1020 steel, and the second of which, designated as frit "B," is designed to fit the high-expansion alloy steels suitable for use under high temperature conditions.

Frit "A"

	Parts by weight
Quartz	24.4
Feldspar	35.0
Borax	23.9
Soda ash	6.4
Soda niter	4.1
Fluorspar	3.7
Cobalt oxide	.5
Nickel oxide	.5
Manganese oxide	1.5
	100.0

Frit "B"

	Parts by weight
Quartz	24.6
Feldspar	35.2
Borax	14.7
Soda ash	15.0
Soda niter	4.2
Fluorspar	3.8
Cobalt oxide	.5
Nickel oxide	.5
Manganese oxide	1.5
	100.0

The frits are prepared in the conventional manner, i. e., the materials are weighed out in the amounts indicated in the above composition formulas, mixed together, and screened through a 20-mesh sieve. The sieved material is then thoroughly mixed and melted to complete fusion as indicated by a smooth thread. The melt is then quenched in cold water and dried and the frit is ready for use.

The mill batch is prepared by the addition of diaspor to frit "A" or to frit "B" depending on whether the coating is to be used on a metal having a relatively low coefficient of expansion or on a metal having a relatively high coefficient of expansion. While a very suitable mill addition for use with either of the above frits may consist of a suitable amount of first grade diaspor ground up with the frit and the proper amount of water and electrolytes to form a slip of the proper consistency, it has been found that in base coatings designed for high temperature durability in which the viscosity may be relatively high, a minute bubble structure is desirable to increase the resistance of the coating to fish-scaling. It has been found that small additions of sodium carbonate will produce the fine bubble structure but will, at the same time, violently flocculate the plastic particles of clay ordinarily used as a suspending medium. This difficulty, however, may be overcome by the use of a 200-mesh flint fire-clay which is of rather low plasticity and gives an entirely suitable consistency to the coating slip in the presence of sodium carbonate. Accordingly, the formulas for two mill batches will be set out below, the first batch being

4

designated as mill batch "A" and consisting of diaspor, borax, and water, while the second batch, which is designated as mill batch "B" consists of diaspor, flint clay, soda ash and water and may be found useful to prevent fish scaling of the coating by reason of the minute bubble structure formed within the coating.

Mill batch "A"

	Parts by weight
Frit "A" or "B"	65.0
Diaspor (1st grade)	35.0
Borax	0.75
Water	50.0

Mill batch "B"

	Parts by weight
Frit "A" or "B"	65.0
Diaspor (1st grade)	35.0
Flint clay	5.0
Soda ash	4.0
Water	50.0

The mill batch is prepared by measuring out the proper amounts of frit, diaspor, water, etc., and placing them together in a ball mill for grinding. The batch is ground in the mill until a 2 to 4 gram dry residue remains on a 200-mesh screen from a 100 gram sample of slip. The slip is then ready for application to the metal to be coated.

In order to secure best results the metal should be prepared for coating by first annealing the metal from 3 to 15 minutes at 1200 to 1300° F., after which it is thoroughly cleaned of any carbon scale or other deposits by sandblasting. In the case of metals which lend themselves to cleaning by a pickling process, this method may be used in lieu of the annealing and sandblasting process.

The metal thus prepared is then coated with the slip by dipping the metal into the slip and draining off the excess or by spraying the slip onto the metal. A slip made in accordance with the formulas given above should be adjusted by the addition of suitable electrolytes to have a pick-up of about 40 grams dry weight per square foot upon dipping, which will give a coating 3 or 4 mils thick. This thickness of coat has been found to be very satisfactory for #1020 steel, though a somewhat thinner coat may be found more suitable for use on alloy steels having a very high coefficient of expansion. The coating is dried according to standard practice in a hot air drier after which the coated article is placed in an enameling furnace and fired at 1750° F. until adherence is obtained. This has been found to require from five to ten minutes for 16-18 gauge metal. Heavy sections of metal, such as lugs, welds, etc., require a somewhat longer firing time in order to mature the coating.

The resulting coating will be found to possess a very remarkable degree of adherence to the metal and will withstand a considerable amount of rough handling and abuse. It will also adhere firmly to the metal in spite of repeated severe thermal shocks, as mentioned earlier in the description. Probably its most remarkable quality, however, is its ability to protect the metal at temperatures in the neighborhood of 1500° F. for long periods of time, which, as earlier pointed out, is largely due to the presence of diaspor in the composition. The coating will prevent oxidation of the metal at these high temperatures and will also tend to insulate the metal from the extreme heat of the exhaust gases.

5

By virtue of its excellent adhering and protective qualities, the above-described coating may be very advantageously used as a base coat over which a subsequent top coat may be applied. This top coat may be designed to supply additional desirable qualities to the coating and thus further enhance the utility of the coating. For example, the radiation suppressive top coats described in our copending application Serial No. 628,360 filed November 13, 1945, and entitled "Ceramic coating material" will be found to yield very excellent results when applied over the present base coats both from the standpoint of affording additional protection to the metal and also from the standpoint of reducing the visible and infra-red radiations therefrom.

It is thought that the essential features of the invention are fully defined by the foregoing description, but it will be understood that any modifications or alterations in the materials employed or in the proportions of the materials employed which fall within the scope of the appended claims may be utilized without departing from the spirit of the invention.

We claim:

1. In combination, a supporting layer of the steel designated by the United States Society of Automotive Engineers as No. 1020, and firmly attached to said steel layer, an enamel coating which is a fusion product of a frit comprising

Parts by weight

Quartz	24.4
Feldspar	35.0
Borax	23.9
Soda ash	6.4
Soda niter	4.1
Fluorspar	3.7
Cobalt oxide	0.5
Nickel oxide	0.5
Manganese oxide	1.5

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and a mill addition comprising first-grade diaspore, flint clay, soda ash and water, the parts by weight of the mill addition being in the same units of weight as the parts by weight of the frit, the proportions of the said materials being as follows:

Parts by weight

Frit	65.0
Diaspore (1st grade)	35.0
Flint clay	5.0
Soda ash	4.0
Water	50.0

6

said combination having been applied to the steel in such a condition of fineness that it will pass substantially entirely through a standard 200 mesh screen and fired on the steel at a temperature of about 1750° F. for at least ten minutes and for such a length of time until good adherence has been obtained.

2. The combination which comprises a base layer of a high expansion alloy steel suitable for use under high temperature conditions upon which there is fused an enamel in such a manner that it will withstand great thermal shock without separating from the steel layer, said enamel consisting of a fused composition as follows:

Parts by weight

Frit	65.0
Diaspore (1st grade)	35.0
Flint clay	5.0
Soda ash	4.0
Water	50.0

the frit therein consisting of

Parts by weight

Quartz	24.6
Feldspar	35.2
Borax	14.7
Soda ash	15.0
Soda niter	4.2
Fluorspar	3.8
Cobalt oxide	0.5
Nickel oxide	0.5
Manganese oxide	1.5

100

the parts by weight of the mill addition being in the same units of weight as the parts by weight of the frit, said enamel having been fused to said steel and at a temperature of about 1750° F. for at least ten minutes and for a sufficient length of time to obtain good adherence.

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