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ENAMEL COMPOSITION

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1 Claim. (CL 106—48)

The present invention relates to new and useful improvements in vitreous enamel compositions.

Heretofore it has long been the custom in the production of vitrified enamels to smelt into the enamel certain substances to promote adherence of the enamel to the ferrous base metal when it is applied to the surface and fired. These substances have been cobalt oxide, either alone or in conjunction with nickel oxide and/or manganese oxide. Such a frit produces a dark blue ground coat which is usually covered with other enamels containing opacifiers in order to leave the product with a white or light colored finish. The usual practice is to apply two such coats, as it has been found that one heavy coat is insufficient to completely cover the dark colored ground coat, so that in the production of enamel ware three distinct coats, and thus three distinct heat treatments, are necessary for a finished product of the desired quality.

It has been proposed to smelt about 1.5% molybdenum trioxide (MoO_3) and 7.5% antimony oxide (Sb_2O_3) with a typical enamel batch from which the dark-color producing substances cobalt oxide, nickel oxide, and manganese oxide have been omitted and thus to produce a light colored ground coat which would have the necessary adherence properties. However, it was found that the results were erratic and satisfactory adherence was frequently not attained, probably due to the volatilization of the added oxides during the smelting of the frit. It has also been proposed to electroplate the ferrous base with $\text{MoO}_3 \cdot x\text{H}_2\text{O}$ to promote adherence, but this requires accurate control and added equipment, as well as entailing an operation which is foreign to the usual enamelling process.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the steps, instrumentalities and combinations pointed out in the appended claim.

The invention consists in the novel steps, processes, combinations and improvements herein shown and described.

The present invention has for its object the provision of a new vitreous enamel composition which is more adherent to the base metal on which the enamel is applied and fused. The in-

vention also provides a vitreous enamel composition which requires a fewer number of coats, and is of a white or light color. A further object is to provide such a composition which reboils very slightly, which makes possible the use of lower temperatures in the fusion of ground coats for enamel ware, and permits finer adjustment of the ground coat at the mill.

In accordance with the present invention the adherence of the enamel coating may be promoted and the opacity of light colored coats improved by the use of molybdenum salts and compounds in any type of enamel frit or ground coat mixture. The molybdenum is usually employed in connection with antimony oxides and the molybdenum compounds may be added to the smelt when the frit is produced or milled in with the enamel when preparing the slip, depending upon the type of compound used and the results desired. When light colored coats are desired, the usual smelted in cobalt, manganese, and/or nickel oxides may be omitted and the molybdenum and antimony compounds employed, the other ingredients of the usual enamel frit being used in substantially the same proportions. The first coat adheres at least as well as the cobalt-nickel-manganese frit heretofore used, and has the added advantage that due to the light color and opacity only one additional coat is required to completely obscure the base.

It will be understood that the foregoing general description and the following detailed description as well, are exemplary and explanatory of the invention but are not restrictive thereof.

Referring now in detail to several illustrative methods of preparing the compounds and carrying out the processes of the present invention, a molybdenum suboxide, such as molybdenum dioxide (MoO_2) or "molybdenum blue," is milled with antimony trioxide (Sb_2O_3) in a clear frit, has been found to produce excellent adherence when fused on the ferrous base metal and, probably due to the fact that it is insoluble in the mill liquor, there is no crawling, tearing or peeling of the enamel during the firing process.

Successful results have been obtained throughout a considerable range of variation in the amounts of a lower oxide of molybdenum and antimony trioxide (Sb_2O_3) used, and the proper amounts will depend on a number of circumstances, such as, for example, the nature of the enamel, the nature of the iron surface, the thick-

ness of the coating, and furnace conditions, and the amounts actually used in practice should be determined experimentally for each set of conditions. In general, however, it has been found that excellent adherence is attained when the proportion by weight to the frit of MoO_2 is from 0.25 to 5.0% and of Sb_2O_3 is from 0.25 to 15.0%. Experiments tend to show that the best adherence is generally associated with substantially two parts by weight of Sb_2O_3 to one part by weight of MoO_2 , and it is probable that the best theoretical proportion is the proportion of the atomic weights of the compounds, i. e., 291.52 parts Sb_2O_3 to 127.75 parts MoO_2 , in accordance with the reaction theory as hereinafter set forth. Thus the use of 2.92% Sb_2O_3 and 1.28% MoO_2 has shown excellent results, although at times "antimony blisters" are produced, but this is entirely eliminated by the addition of a slight excess of MoO_2 .

Molybdenum trioxide (MoO_3) may likewise be used as a mill addition to a clear enamel base along with antimony trioxide (Sb_2O_3) to produce a white or light colored ground coat with excellent adherence to the ferrous base metal. With these substances better adherence is obtained when the amount of MoO_3 is varied between 1% and 2%, and the Sb_2O_3 between 1% and 4%, and here again the best results are associated with the proportion of substantially two parts by weight of Sb_2O_3 to one part by weight of MoO_3 , with the ideal theoretical proportion probably being the relation of the molecular weights, i. e., 291.52 parts Sb_2O_3 to 143.95 parts MoO_3 .

Antimony molybdate ($\text{Sb}_2\text{O}_3 \cdot \text{MoO}_3$) has proved to be an excellent adherence producing agent, and it may be milled with a clear enamel base in amounts varying from 3% to 4% in order to produce the best results. Its use imparts a brownish-yellow color to the enamel so that MoO_2 and/or MoO_3 used with Sb_2O_3 are to be preferred when a white enamel is desired.

Excellent adherence may be obtained by the use of the barium antimony molybdates, and these are advantageous for the reason that the antimony and molybdenum oxides are thus used in a very insoluble form. $2\text{BaO} \cdot \text{Sb}_2\text{O}_3 \cdot \text{MoO}_3$ produces a white enamel, while a yellow enamel may be obtained by the use of $\text{BaO} \cdot \text{Sb}_2\text{O}_3 \cdot \text{MoO}_3$, and a yellow-brown color by use of



Calcium antimony molybdate



will also produce a yellow-brown color in the enamel.

The use of molybdenum compounds is not limited to their addition to a prepared frit in the milling operation where the final slip is prepared. They may also be used as an initial ingredient in the smelting of the frit. Thus complex salts and compounds of molybdenum which yield a suboxide of molybdenum on being heated to relatively high temperatures such as are employed for enamelling, such as the salts of ammonia and the amines may be added directly to the smelt, and the suboxides of molybdenum will be formed during the smelting operation and be an ingredient of the finished enamel.

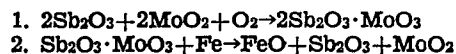
The use of such complex compounds of molybdenum either as mill additions or as enamel ingredients has been found to have the additional advantage that when heat is applied and a suboxide of molybdenum produced, it will be pres-

ent in the slip in very finely divided form, and thus the necessity for extremely careful grinding is avoided as when the suboxides are milled in with the enamel. Thus the present invention has been found to yield excellent results when antimony oxide is smelted into the enamel batch, and ammonium molybdate added during the milling operation.

While the invention has been disclosed in certain preferred embodiments using a suboxide or trioxide of molybdenum together with antimony trioxide, or using antimony molybdate alone, as mill additions to enamel, or using certain compounds of molybdenum in the preparation of enamels, and certain other compounds have been suggested, it will be understood that said embodiments are merely examples of the invention, and are not to be taken as limiting or defining the larger application of the invention as a whole. Thus, results within the scope of the present invention may be obtained by the use of any of those substances separately, as well as by the use of other antimony and molybdenum compounds either separately or in combination. For instance, sodium antimoniate and molybdenum dioxide, calcium antimoniate and calcium molybdate, or antimony oxide and calcium molybdate may be used as mill additions to the ground coat enamel. Complex compound such as molybdenum blue, which may be represented by the formula $x\text{MoO}_2 \cdot y\text{MoO}_3 \cdot z\text{H}_2\text{O}$ produce excellent opacity and adherence.

The alkali, alkaline earth, ammonium, amine, zinc, lead and other metallic salts of the molybdenum acids may be used as the source of molybdenum, and likewise the antimonates of the alkali metals, alkaline earth metals, ammonium, zinc, lead and cadmium, as may be the complex antimonate and arseno-molybdates of calcium, zinc, lead and cadmium, and the like.

Experiments have tended to show that the principal factor which influences the adhesion of enamels to iron is the presence of oxygen-carrying agents in enamel. Cobalt and nickel compounds as heretofore used in enamel batches are understood to absorb oxygen from the air and give it up to the iron base. It is believed that molybdenum and antimony compounds used in accordance with the present invention also do this. Thus, when a light-colored ground coat, containing milled-in Sb_2O_3 and MoO_2 is heated in contact with iron, the following reactions may occur:



In the early stages of firing, before the enamel fuses, MoO_2 absorbs oxygen to form MoO_3 , which combines with Sb_2O_3 to form antimony molybdate ($\text{Sb}_2\text{O}_3 \cdot \text{MoO}_3$). Two functions are served by this reaction: (a) by rapidly absorbing atmospheric oxygen, excessive primary oxidation of the iron base may be prevented, and (b) by forming the very fusible antimony molybdate, the unfused coating tends to become vitrified, thereby diminishing further primary oxidation of the base.

The iron base is oxidized by the liberation of some of the available oxygen in the antimony molybdate, and the antimony molybdate then is regenerated by oxygen carried into the glass from the furnace atmosphere. This reaction is probably cyclical, continuing throughout the firing period, and the oxidation of the iron base takes place continuously under the fused glassy

coating. It has been observed that adherence is adversely affected by the use of opacifiers in the ground coat, and that successful ground coats must have good fluidity, and these facts are probably due to the necessity of having atmospheric oxygen easily available for the above reactions occurring at the surface of the iron.

It will be understood that the foregoing discussion of reactions is only a possible and reasonable explanation of the observed results of the present invention, is empirical only, and is not to be understood as limiting the scope or application of the invention.

In addition to the presence of oxygen-carrying agents in the enamel, and good fluidity of the milled material when it is placed upon the metal surface to be fired, it has been found that a third factor essential for the adherence of an enamel ground coat is a surface free from grease, oil or dirt. The degree of pickling or etching of the surface which should be affected depends upon the oxidizing conditions which will be encountered in the firing process. When a laboratory furnace is to be used having a slow comeback, deep etching is necessary to bring about maximum adherence. In industrial furnaces, both box and continuous, where severe oxidizing conditions and rapid heat transference occur, lighter pickling is sufficient for good adherence.

When the present invention is practiced by using the molybdenum compounds as mill additions, a number of different enamel batches may be used to produce the frit. In general, any cobalt enamel batch with the coloring oxides omitted may be used, and different batches may be chosen in order to secure ground coats with different heats of fusion. Thus a typical smelter batch to produce ground coats maturing at 1580 to 1600° F. is:

	Per cent
Borax	35.5
Feldspar	26.0
Quartz	20.5
Soda ash	6.6
Soda niter	5.3
Fluorite	6.1
	100.0

and such a frit may be used as the basis of a mill batch addition of molybdenum, as follows:

	Grams
Frit	1000
Clay	70
Borax	5
Antimony trioxide	12.5
Calcium molybdate	12.5
Water	550

or 7.5 g. molybdenum trioxide may be substituted for the calcium molybdate.

A small amount of antimony oxide may be smelted-in, in which case the batch is:

	Per cent
Borax	34.4
Feldspar	25.0
Quartz	19.8
Soda ash	6.4
Soda niter	5.1
Fluorite	5.8
Antimony trioxide	3.5
	100.0

To this melted batch, the other ingredients may be added in the following proportion:

Frit	1000
Clay	70
Borax	7.5
Calcium molybdate	12.5
Water	550

and 7.5 parts of $(\text{NH}_4)_2\text{MoO}_4$ may be substituted for the calcium molybdate with good results.

A softer ground coat, which may be used at 1500° F. or lower is:

	Per cent
Borax	47.4
Feldspar	17.3
Quartz	16.8
Soda ash	4.9
Soda niter	2.7
Barium carbonate	6.1
Fluorite	4.8
	100.0

This is then smelted, milled, and the following milled in:

Frit	1,000
Clay	70
Borax	5
Antimony trioxide	10
Calcium molybdate	15
Water	550

This batch, also, may contain smelted-in antimony trioxide, and the firing range will be the same:

	Per cent
Borax	45.8
Feldspar	16.7
Quartz	16.2
Soda ash	4.7
Soda niter	2.5
Barium carbonate	5.9
Fluorite	4.7
Antimony trioxide	3.5

	100.0
Frit	1,000
Clay	70
Borax	5
Ammonium molybdate	10
Water	550

(15 parts lead molybdate may be substituted for the ammonium molybdate.)

In general the frits are milled in the usual manner to about 8 grams on 200 mesh for a 100 gram sample, a typical mill batch being

Frit	1,000
Vallendar clay	70
Borax	5
Water	550

and the adherence promoting compounds are added and milled-in in the amounts heretofore discussed.

These enamel batches or others may likewise be used when the molybdenum compound is smelted directly into the frit.

Although it is not essential to the success of the process, it has been found that the gloss and texture as well as the uniformity of the enamel is promoted when the desired amounts of adherence promoting compounds, Sb_2O_3 and MoO_3 , for instance, are wet milled together and then dried before addition to the mill batch for grinding with the frit.

Other specific examples of enamels illustrative of the present invention are the following:

WHITE GROUND COAT AT 1550° F.

Smelter batch		Mill batches	
	Per cent		
Borax	28.75	Frit	1,000
Feldspar	25.20	Clay	60
Quartz	19.90	(NH ₄) ₂ MoO ₄	7.5
Cryolite	12.65	Water	500
Soda ash	1.60	or	
Soda antimoniate	5.81	Frit	1,000
Fluorite	3.53	Clay	60
Soda niter	2.56	PbMoO ₄	12.5
		Water	500
	100.00		

ONE-COAT WHITE ENAMEL AT 1550° F.

Smelter batch		Mill batches	
	Per cent		
Borax	27.6	Frit	1,000
Feldspar	24.2	Clay	60
Quartz	19.1	(NH ₄) ₂ MoO ₄	6
Cryolite	12.1	Water	450
Sodium antimoniate	11.2	or	
Soda niter	2.4	Frit	1,000
Fluorite	3.4	Clay	60
		Sodium nitrite	3
		PbMoO ₄	20
		Water	450
	100.0		

While the invention has been described with considerable particularity as applied to ground coats, and the preferred composition for carrying it out have been disclosed, it will be appreciated by those skilled in the art that the invention is of wider application, is applicable to sheet steel cover coat enamels, hollow-ware enamels and cast iron enamels as well, and that other compositions than those described may be used. Reference is therefore to be had to the appended claim for a definition of the limits of the invention.

What I claim is:

The process of enamelling iron metal ware, comprising milling the frit with an oxide of molybdenum and with an oxide of antimony, the amount of the molybdenum oxide with relation to the frit being from .25 to 5% by weight and the amount of the oxide of antimony being twice the amount of the molybdenum oxide, and applying the milled mix to a metal surface and firing it, thereby forming the readily fusible antimony molybdate to give an enamel of good adherence to iron.

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