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PORCELAIN ENAMEL GROUND COAT

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This invention relates, as indicated, to porcelain enamel ground coats, so referred to because the porcelain enamel prepared in accordance with the principles of our invention is particularly adapted for direct application to the work.

The porcelain enamels of the present invention may be employed as single cover coats on the work, however their greatest usefulness will be found as ground coats for direct application to the work and over which a subsequently fired cover coat is provided.

It is among the objects of our invention to provide porcelain enamels of the character described which are an improvement over the prior art from the standpoint of their cost, their properties after application, and the facility with which the same may be applied.

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

To the accomplishment of the foregoing and related ends, said invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims.

The following description sets forth in detail one approved method of carrying out the invention, such disclosed method, however, constituting but one of various ways in which the principle of the invention may be used.

Our invention, broadly stated, comprises the discovery that an improved porcelain enamel may be provided and one which is particularly applicable for direct application to the work by first producing a slip in which porcelain enamel frit is ground to a particular fineness and employed in conjunction with certain other materials of specified properties and fineness.

More specifically, our invention comprises the discovery that an improved porcelain enamel which is particularly suited for direct application to metallic surfaces may be provided by employing in conjunction with the frit constituents of the slip substantial amounts of finely ground filler material, preferably siliceous in nature, containing substantially no volatile material and being substantially infusible in the temperature range where the frit is fusible. A slip thus prepared is applied to the work in the customary manner and then fired in the temperature range of fusibility of the enamel frit.

For a full understanding of our invention it is believed desirable to separately refer to the various components which make up the slip which is employed in carrying out the principles of our invention.

The frits

There are many frits available at the present time which may be employed in carrying out the principles of our invention. Since our improved porcelain enamel is designed particularly for direct application to the work and more particularly metallic surfaces, the frit selected should be of such character as is suitable for direct application to the work. In general, any conventional frit which contains a sufficient amount of bonding oxides such as cobalt oxide, for example, may be employed in our invention. We are aware of the fact of course that expedients for promoting bond other than the inclusion in the frit of so-called bonding oxides have been proposed and have met with some degree of success. Our invention is applicable to frits of such character as well.

For purposes of description of the present invention we shall classify the various frits which may thus be employed in accordance with their respective fusion ranges.

By "fusion range" as employed throughout this specification and in the appended claims is meant that temperature range at which the frit may be successfully fired onto a metallic surface.

Frits which have a relatively high fusion range or firing range are generally referred to as hard frits, and those which have a relatively lower fusion or firing range are commonly referred to as soft frits. Throughout the following description and in the appended claims where reference is made to the combined use of both hard and soft frits in a single slip it is intended that whole the actual fusion or firing range of the two frits may actually overlap, nevertheless the lower limits, for example, of the respective ranges are different on the order of about 25° to 100° F. Instead of merely using two such frits in combination, any practical number may be thus combined and in this way properties heretofore impossible achieved by such combination.

In order to assist those skilled in the art in selection of hard and soft frits we set out hereinbelow a formula for each of such frits.

	Soft	Hard
Feldspar	32.24	40.50
Quartz	26.75	25.20
Borax (anhydrous)	24.47	23.28
Sodium nitrate	3.50	5.00
Soda ash	8.68	7.39
Fluorspar	6.50	2.00
Limestone	3.57	.....
Cobalt oxide	.50	.53
Black Ni oxide	.79	1.45
Manganese dioxide	1.66	1.12

The figures given in the foregoing table are parts by weight.

The filler material

It is an important feature of our invention that we employ in the enamel producing slip, along with one or the other or mixtures of hard and soft frits, a material which we shall for convenience designate as a filler material. This filler material may be any inorganic material substantially free from volatile matter (water or other volatile substances) and which is substantially infusible in the temperature range within which the slip is fired, i. e. the fusion range of the frits comprised in the slip.

This filler material should be relatively inert, i. e. it should not react with the slip constituents at least to the extent that these filler materials shall not be incompatible with the slip constituents. Among the materials which are generally available for this purpose are silicate, quartz and feldspar.

Other slip constituents

Obviously the frits and filler materials must be combined with other materials in the production of a slip which may be satisfactorily applied to and fired on the work. Any conventional electrolyte may be employed and any conventional suspending medium, water being preferable for reasons well known. Various slip conditioning constituents may likewise be added such as clay, barium hydroxide, etc., for the purpose of properly conditioning the slip and for the purpose of maintaining the frit and filler materials in suspension and proper distribution during the process of applying the slip to the work.

Particle size

The particle size of the frit and filler materials which enter into the slip is of major importance. A reduction in the particle size to such extreme fineness that on the order of about 95% will pass through a 325 mesh screen is of assistance in general in increasing the covering power of the enamel and within certain limits in increasing the bond. We have found, however, that in general grinding the frit much finer than 90% through a 325 mesh screen does not increase, but instead tends to decrease the bonding properties of the enamel.

It might be well at this point to indicate what is meant by the terms defining "fineness" as employed in this specification and in the claims. When we refer to a fineness such that substantially all will pass through a 200 mesh screen for example, we mean a fineness such as is obtained by grinding the constituents in a conventional ball mill to such an extent as is obtained by continuing the grinding operation only slightly beyond the time required to produce a fineness which is such that there is at least a 1% residue on the screen. The same definition of course applies in connection with reference to finenesses which will pass a 325 mesh screen.

Extremely fine grinding, i. e. to the extent that on the order of about 95% will pass through a 325 mesh screen, as indicated, increases the covering power of the enamel and accordingly makes it possible to secure adequate coverage with considerably lesser weights of application. Ground coats are to-day milled to a fineness such that about 85% to about 90% will pass through a 200 mesh screen. If now the milling is continued and the fineness reduced so that about 90% will pass through a 325 mesh screen, coverage comparable to that secured at present may be achieved with amounts as little as 50% to 60% of conventional weights of application.

Fine grinding the enamel is, however, not the complete answer to the problem of providing a satisfactory enamel for direct application to the work.

By incorporating in the enamel substantial quantities ranging from about 10% to about 50% of the amount of frit of a filler material as previously defined, we are able to achieve results which have heretofore not been produced.

Particle size of the filler material and the relation of such particle size to the particle size of the frit are important factors. In accordance with our invention the filler material should be reduced to a particle size generally finer than that of the frit.

The degree of fineness to which the two constituents, i. e. the frit and the filler material, should be ground can best be explained by having reference to the function of the filler material. In the first place, grinding the entire slip to extreme fineness such that all will pass through a 325 mesh screen is not desirable since such a reduction in particle size interferes with the draining properties of the slip when applied to the work by dipping. A certain percentage of relatively coarse particles are necessary in order that the slip may have the necessary draining properties. The slip should, however, contain a sufficient proportion of more finely divided particles so that they may fill the voids of the coarser constituents. By combining substantial proportions of extremely fine ground filler material with frit of medium fineness we secure most, if not all, of the advantages which accrue from extremely fine ground frit, with none of the disadvantages incidental to a division of the frit particles themselves to extreme fineness.

The relative degree of fineness of the two constituents, i. e. the frit and the filler material, may be regulated in two ways, either by separately dry grinding the frit and the filler material to the specified degree of fineness and then combining the same as a dry mix or by pre-milling one or the other or both of such constituents to a particular degree of fineness and then milling a mixture of the same for a predetermined length of time. If the latter expedient is to be adopted then of course the filler material should be premilled to a greater degree of fineness than the frit at the time the two constituents are admixed preparatory to further dry grinding.

The manner in which this reduction in particle size is achieved is also important. It is customary in the industry at the present time to place the pea size frit in a ball mill with the necessary amount of electrolyte and other slip conditioning agents and then wet mill the mixture until the desired fineness is achieved. The amount of wet milling thus necessary in the presence of the water results in there being dissolved in the water substantial amounts of the components of the frit complex. If an attempt were made to fine grind in the wet state down to a point where on the order of about 95% would pass through a 325 mesh screen the amount of the frit components dissolved in the water would become so great as to not only unbalance the frit complex but to very decidedly interfere with the setting up and other handling properties of the slip as to be impractical. For this reason we have found it preferable to grind the frit to substantial fineness in the dry state, carrying on the wet grinding operation only to the extent necessary to secure an intimate mix-

ing and conditioning of the slip. Since grinding times up to six hours in the wet state will generally not result in too great a "solubility" of the frit constituents in the water, it is possible to effect the reduction in particle size to the extent possible by such grinding time.

As previously indicated, the relative particle sizes of the frit and filler material should be different in the final slip. Such constituents should, therefore, be preground in the dry state either separately or in admixture, as above explained, to an extent such that reduction to the final desired particle size may be accomplished by a wet milling during the period not to exceed six hours.

We have been able to secure unexpectedly improved results by employing a combination of different frits in the slip. In particular, we have been able to secure unexpectedly improved results by thus combining frits which have respective firing or fusion ranges which may differ as much as about 100° F.

When employing this combination of frits of different firing or fusion ranges, we have also secured unexpectedly improved results by grinding the different frits to different degrees of fineness. In general, it will be found that superior results are secured when the hard frit is ground substantially finer than the soft frit. The projections within which the relatively hard and soft frits may be combined vary from about 1 to 4 to about 4 to 1. In general, superior results will be secured if the relatively hard frit is employed in the majority and the relatively soft frit is employed in the minority within the above stated range. Excellent results are secured when the two frits are employed in equal proportions.

The following will serve to illustrate different ways by which a finished slip prepared in accordance with our invention may be made.

The frit, whether a single frit or a combination of hard and soft frits, are dry ground so that on the order of about 95% will pass through a 200 mesh screen. The filler material is dry ground to a fineness such that on the order of about 80% will pass through a 325 mesh screen. The premilled frit and filler material are then combined in proper proportions in a wet mill along with appropriate amounts of slip conditioning agents and water and wet ground for a period of time sufficient so that 85% to 95% of the slip will pass through a 325 mesh screen.

Another slip may be prepared by dry grinding the frit whether it be a single frit or a combination of hard and soft frits in the proportions stated to a fineness such that on the order of about 45% will pass through a 200 mesh screen. The filler material is dry ground to a fineness such that on the order of about 98% to 100% will pass through a 325 mesh screen. These premilled constituents are then combined in a wet mill along with sufficient amounts of slip conditioning agents and water and ground for a length of time sufficient so that from about 92% to about 98% of the slip will pass through a 200 mesh screen.

A further example of the slip prepared in accordance with our invention and one which utilizes a combination of hard and soft frits respectively ground to different degrees of fineness may be prepared by dry grinding a hard frit to a fineness such that about 80% will pass through a 325 mesh screen; dry grinding a soft frit so that on the order of about 45% will pass through a 200 mesh screen. The filler material is dry ground to a fineness such that on the order of about 95% will pass through a 200 mesh screen. Appropriate proportions within the ranges herein given of the premilled hard and soft frits and the filler material are then combined in a wet mill along with a sufficient amount of slip conditioning agents and water and milled for a length of time sufficient so that about 95% to about 98% of the slip will pass through a 200 mesh screen.

As above indicated, improved results will be secured with certain combinations of hard and soft frits when the hard frit is ground finer than the relatively soft frit. In one particular instance very excellent results have been secured by employing a hard frit in amounts of about 70 parts by weight ground to a fineness such that about 95% will pass through a 325 mesh screen in combination with about 30 parts by weight of a relatively soft frit ground to a fineness such that about 87% will pass through a 200 mesh screen. This combination is of course employed in conjunction with filler materials of the character described and within the proportions previously given and such filler materials should be ground at least as fine and preferably finer than the finest of the two frits.

At this point it may be well to again note that the fineness of the filler material is also a condition which should be rather carefully observed, to the extent at least that while it is generally essential to have the filler material ground substantially finer than the frit, filler material of colloidal or even semi-colloidal particle size is not suitable for use in our invention.

A slip prepared in the manner above stated will generally be found to work best if the amount of water is so adjusted that the specific gravity of the slip lies between 1.50 and 1.67, this being determined, however, to a considerable extent by the manner in which the slip is to be applied to the work. The slip may be applied to the work either by brushing, spraying or dipping. The slip mixture comprising our invention, or more particularly a mixture of the two principal constituents, i. e. the frit and the filler material, will also be found to be useful for application to the work by means of a heated spray such as is produced by an acetylene flame and which flame melts the material as it is deposited on the work. The usual precautions observed in the preparation of the material for application to the work in this manner should be observed when employing our mixture of enamel forming constituents.

The slip thus prepared and applied to the work is fired, preferably at a temperature which lies between the fusion ranges of the two frits when a mixture of frits is employed and within the fusion range of the single frit when only one is employed.

It is important to note that in carrying out our invention the factors of relative particle size of the frit and filler material and relative proportions of such materials employed is such that there is substantially no change in the temperature range at which the slip may be fired. That is, our invention will be distinguished over prior uses of filler material of such particle size and in such proportions as to make the firing range of the slip very substantially different from the fusion range of the frit.

During the firing operation the fusion of the frit serves as a bonding material for the filler material which has been added as well as a bonding material for the entire ceramic mass to the work to which the same is applied. Due to the na-

ture of the enamel as thus prepared it will be found that when the same is applied directly to a metallic surface, for example, the enamel will have excellent covering power and bond and be noticeably free from air cracks, tearing and "copperheading."

A further and very important property of our enamel is that it will be found to possess greater stability after the initial firing and during subsequent refiring, that is when a cover coat is fired thereon. The ground coats of our invention have less tendency to reboil than the ground coats which have been previously produced.

Another very desirable property is that since the addition of the filler material broadens the firing range of the enamel and fine grinding lowers and also broadens the firing range, the element composition will be found to have a desirably broad and low firing range as compared with ground coats of the prior art.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the process herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to the base material, which comprises providing a porcelain enamel frit of a composition suitable for direct application to the base material, preparing a slip which comprises a uniform mixture of such frit reduced to a fineness of from about 85% through a 325 mesh screen down to about 95% through a 325 mesh screen and from about 10% to about 50%, based on the amount of frit, of a siliceous material substantially free of volatile matter, substantially infusible in the fusion range of the frit and of a generally smaller particle size than that of the frit, applying such slip to the work and firing the same in the fusion range of the frit.

2. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to a metallic base, which comprises providing a porcelain enamel frit of a composition suitable for direct application to a ferrous surface, preparing a slip which comprises a uniform mixture of such frit reduced to a fineness of from about 85% through a 325 mesh screen down to about 95% through a 325 mesh screen and from about 5% to about 50%, based on the amount of frit, of a siliceous material substantially infusible in the fusion range of the frit and of a particle size generally smaller than that of the frit, applying such slip to the work and firing the same in the fusion range of the frit.

3. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to the base material, which comprises providing a porcelain enamel frit of a composition suitable for direct application to the base material, preparing a slip which comprises a uniform mixture of such frit reduced to a fineness such that from about 85% to about 98% will pass through a 200 mesh screen and from about 5% to about 50%, based on the amount of frit, of material substantially free of volatile matter, substantially infusible in the fusion range of the frit and of a fineness such that about 98% to 100% will pass through a 325 mesh screen, applying such slip to the work and firing the same in the fusion range of the frit.

4. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to the base material, which comprises providing a porcelain enamel fruit of a composition suitable for direct application to the base material, preparing a slip which comprises a uniform mixture of such frit reduced to a fineness of from about 85% through a 325 mesh screen down to about 95% through a 325 mesh screen and from about 5% to about 50%, based on the amount of frit, of a material selected from the class consisting of silica, quartz and feldspar of a generally smaller particle size than that of the frit, applying such slip to the work and firing the same in the fusion range of the frit.

5. In the art of porcelain enameling, the process of providing a coat of porcelain enamel which comprises providing a plurality of porcelain enamel frits of compositions differing in the limits of their respective fusion ranges by temperatures of from 25° F. to 100° F., preparing a slip comprising a mixture of from about 1 to 4 to about 4 to 1 parts of said different frits reduced to a fineness of from about 85% through a 325 mesh screen down to about 95% through a 325 mesh screen and from about 5% to about 50%, based on the total amount of frit, of a siliceous material substantially free of volatile matter, substantially infusible in the highest fusion range of the frit present, and of a particle size generally smaller than that of the frit, applying such slip to the work and firing the same at a temperature between the limits of the fusion ranges of the frits.

6. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to a ferrous metallic base, which comprises providing a plurality of porcelain enamel frits of compositions suitable for direct application to the surface of the ferrous article and differing in the limits of their respective fusion ranges by temperatures of from 25° F. to 100° F., preparing a slip comprising a mixture of from about 1 to 4 to about 4 to 1 parts of said different frits reduced to a fineness of from about 85% through a 325 mesh screen down to about 95% through a 325 mesh screen and from about 5% to about 50%, based on the total amount of frit, of a siliceous material substantially free of volatile matter, substantially infusible in the highest fusion range of the frit present, and of a particle size generally smaller than that of the frit, applying such slip to the work and firing the same at a temperature between the limits of the fusion ranges of the frits.

7. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to a ferrous metallic base, which comprises providing a plurality of porcelain enamel frits of compositions suitable for direct application to the work and differing in the limits of their respective fusion ranges by temperatures of from 25° F. to 100° F., preparing a slip comprising a mixture of from about 1 to 4 to about 4 to 1 parts of said different frits reduced to a fineness such that from about 85% to about 98% will pass through a 200 mesh screen and from about 5% to about 50%, based on the total amount of frit, of material substantially free of volatile matter, substantially infusible in the highest fusion range of the frit present, and of a fineness such that about 98% to 100% will pass through a 325 mesh screen, applying such slip

to the work and firing the same at a temperature between the limits of the fusion ranges of the frits.

8. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to a ferrous base, which comprises providing a plurality of porcelain enamel frits of compositions suitable for direct application to the work and differing in the limits of their respective fusion ranges by temperatures of from 25° F. to 100° F., preparing a slip comprising a mixture of about equal parts of said different frits reduced to a fineness such that from about 85% to about 98% will pass through a 200 mesh screen and from about 5% to about 50%, based on the total amount of frit, of material substantially free of volatile matter, substantially infusible in the highest fusion range of the frit present, and of a fineness such that about 98% to 100% will pass through a 325 mesh screen, applying such slip to the work and firing the same at a temperature between the limits of the fusion ranges of the frits.

9. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to a ferrous surface, which comprises providing a plurality of porcelain enamel fruits of compositions suitable for direct application to the work and differing in the limits of their respective fusion ranges by temperatures of from 25° F. to 100° F., preparing a slip comprising a mixture of from about 1 to 4 to about 4 to 1 parts of said different frits, the frit of the relatively higher fusing range reduced to a fineness such that from about 85% to about 95% will pass through a 325 mesh screen and the frit of the relatively lower fusing range reduced to a fineness such that from about 85% to about 98% will pass through a 200 mesh screen, and from about 5% to about 50%, based on the total amount of frit, of material substantially free of volatile matter, substantially infusible in the highest fusion range of the frit present, and of a particle size greater than colloidal but generally finer than that of said high fusing range frit, applying such slip to the work and firing the same at a temperature between the limits of the fusion ranges of the frits.

10. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to a ferrous surface, which comprises providing a plurality of porcelain enamel frits of compositions suitable for direct application to the work and differing in the limits of their respective fusion ranges by temperatures of from 25° F. to 100 F., preparing a slip comprising a mixture of from about 1 to 4 to about 4 to 1 parts of said different frits, the frit of the relatively high fusing range reduced to a fineness such that from about 85% to about 95% will pass through a 325 mesh screen and the frit of the relatively lower fusion range reduced to a fineness such that from about 85% to about 98% will pass through a 200 mesh screen, and from about 5% to about 50%, based on the total amount of frit, of a material selected from the class consisting of silica, quartz and feldspar and of a particle size substantially larger than colloidal but generally smaller than that of the frit, applying such slip to the work and firing the same at a temperature between the limits of the fusion ranges of the frits.

11. In the art of porcelain enameling, the process of providing a coat of porcelain enamel applied directly to the base material, which comprises providing a porcelain enamel frit of a composition suitable for direct application to the base material, preparing a slip which comprises a uniform mixture of such frit reduced to a fineness such that at least 85% will pass through a 200 mesh screen and from about 10% to about 50%, based on the amount of frit, of material substantially free of volatile matter, substantially infusible in the fusion range of the frit and of a generally smaller particle size than that of the frit, applying such slip to the work and firing the same in the fusion range of the frit.

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