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ENAMEL

Alden J. Deyrup, Westfield, N. J., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to certain improved enamel compositions suitable for use in the manufacture of electrical equipment. More particularly, it relates to certain new and improved vitreous enamel compositions having properties which render them particularly suitable for use in the preparation of electrical resistors and similar electrical apparatus.

In the manufacture of electrical resistors it is usual to wind the resistance wire in coil form on a tube of ceramic base material, suitable clips, clamps, ferrules, or other metallic fastenings being provided at the ends in order to secure the resistance wire on the ceramic base, as well as to provide means for establishing electrical contact therewith. Over the entire surface of ceramic base material and resistance wire there is then provided a layer of vitreous enamel which serves to hold the resistance wire firmly in place, insulating the turns from each other and from outside contact. This enamel layer also serves to protect the winding against deteriorating influences, such as those resulting from the presence of moisture, and electrolytes on the wire, as well as those resulting from atmosphere oxidation.

In the past in preparing electrical resistors of this type great difficulties have been encountered in manufacturing an enameled unit which would satisfactorily withstand the severe stresses to which the members are subjected, both during the process in manufacture, and during subsequent service conditions when the resistor is in use. In part, the severe stresses arise from the fact that electrical resistors are power dissipating units and, as commonly employed in most electrical circuits, are required to dissipate a considerable amount of heat developed in the wire by the current of electricity passing therethrough This generation of heat in the wire of the electrical resistor, which may be gradual or, in some cases, very rapid, gives rise to mechanical stresses of the severest sort, these stresses resulting from the differences in thermal conductivities and coefficients of expansion of the various component parts comprising the resistor. Thus the tubular ceramic base, the resistor element proper, the terminal bands or clips, and the vitreous enamel coating positioned thereon, all differ considerably in these two important thermal characteristics and, when heated, mechanical stresses of considerable magnitude invariably result.

The severe stresses are experienced not only during utilization of the electrical resistors, but also during the manufacturing operations wherein it is necessary, in order to mature the enamel thereon, to subject the assembly to successive firing and cooling operations. The heating incident to maturing the enamel, followed by the subsequent cooling step, very often cause failure of the insulating enamel thus destroying the usefulness of the electrical resistor even before it is utilized in electrical apparatus. Moreover, in some electrical equipment such as in aircraft radio equipment, the resistors may be subjected to severe external temperature changes with great rapidity, these changes in temperature due to external influences occurring simultaneously with the stresses produced by the dissipation of heat developed in the resistance wire itself incident to its use as part of the electric circuit. Enamels which when applied to an electrical resistor of this type will successfully withstand the various stresses encountered during manufacture and use, and which will not craze, crack, spall off or break under these stresses have not hitherto been available commercially to American manufacturers of electrical equipment. The high standards required in an enamel of this type will be appreciated when it is understood that even slight cracking, or any similar slight failure of the enamel coating, will expose the resistance wire underneath to electrolytic or other corrosive action, thus causing changes in resistance or failure of the resistor within a relatively short period of time.

One of the standard tests now utilized to determine the suitability of an enameled resistor element involves connecting the resistor in a suitable electric circuit and passing current therethrough under such circumstances that the external temperature of the vitreous coating is raised to one in the neighborhood of 275° C. The heating is then followed by rapid chilling by plunging the resistor into cold water. The test is designed to provide an adequate criterion of how the resistor will withstand severe service conditons and, in practice, a satisfactory enameled resistor should withstand shocks occasioned by a number of consecutive treatments of this kind without damage. Although many enameled wire-wound resistors are regularly manufactured which will withstand less severe tests and less exacting service conditions, at present there is no suitable enamel available for application to wire-wound resistors of all types which will withstand the stresses to which the member is subjected in this test, or service conditions imposing stresses of comparable severity.

It is accordingly one of the objects of this invention to provide new and improved vitreous enamel compositions which may be applied to wire-wound resistors, such compositions not cracking, crazing, spalling off, or exhibiting failure of any type when the resulting enameled resistor is subjected to the foregoing severe test involving repeated heating and quenching. Still another object of this invention is to provide insulating enamels which may be used for coating electrical resistor elements and similar electrical

equipment, which enamels may be readily applied thereto providing satisfactory insulation, the resulting enameled apparatus being characterized by a resistivity to thermal and other stresses of an order never previously attainable. These and still other objects of this invention will be apparent from the ensuing disclosure of certain preferred embodiments thereof.

I have found that enamel compositions containing large amounts of iron oxide, this oxide being fused into the vitreous enamel composition together with the oxides of lead, boron, aluminum and silicon, possess the superior resistance to crazing and to failure by thermal shock which permits their utilization for the specified purposes. Relatively large amounts of iron oxide are present in my improved vitreous enamels or glazes, amounts ranging from 9% to 20% by weight, these amounts being based on the total weight of the enamel composition.

My preferred enamels comprise the oxidic elements listed in the following table, these elements being present in the proportions specified therein. In all cases the percentages are by weight, based on the total weight of the enamel composition.

TABLE I

	Per cent
Iron oxide (Fe_2O_3)	9 to 20
Lead oxide (PbO)	45 to 65
Boric oxide (B_2O_3)	4 to 20
Alumina (Al_2O_3)	3 to 9
Silica (SiO_2)	4 to 15

In addition to the five oxides noted, other ingredients may also be present such, for example, as one or more of the oxides of nickel, cobalt, and chromium. The latter metal oxides when incorporated in the enamel are beneficial in promoting better adhesion to resistor wires containing iron or an alloy thereof. Non-metallic oxides, such as the oxides of phosphorus, may also be present, and are valuable in widening the firing range of the enamel. When these additional ingredients or some of them are incorporated in the enamel they should be present in the amounts indicated below:

	Per cent
Nickel oxide (NiO)	1 to 5
Cobalt oxide (CoO)	1 to 5
Chromic oxide (Cr_2O_3)	1 to 5
Phosphorus pentoxide (P_2O_5)	1 to 4

These percentages are by weight, based on the total weight of the enamel.

In preparing enamels having compositions falling within the limits specified above various batches of raw materials may be melted until substantially homogeneous glassy melts are obtained. Table II lists five batches, batches A to E inclusive, which when melted yield the novel enamels having the calculated compositions given in Table III below.

TABLE II

Weight percentage batch composition

	A	B	C	D	E
Red lead (Pb_3O_4)	48.1	45.7	48.8	54.1	40.5
Boric acid (H_3BO_3)	18.1	17.2	12.2	6.8	30.3
Ferric oxide (Fe_2O_3)	15.7	14.8	12.2	9.5	12.1
Kaolin (39.5% Al_2O_3; 46.5% SiO_2; 14.0% H_2O)	15.1	14.3	15.2	16.8	12.6
Flint (SiO_2)	3.0	-----	3.1	3.4	-----
Cobalt oxide (Co_3O_4)	-----	1.7	1.8	2.0	1.5
Nickel oxide (Ni_2O_4)	-----	1.7	1.8	2.0	1.5
Chromic oxide (Cr_2O_3)	-----	1.7	1.8	2.0	1.5
Ammon. phosphate ($NH_4H_2PO_4$)	-----	2.9	3.1	3.4	-----

In these batches the various amounts of the different constituents are by weight.

The calculated compositions resulting from melting these batches are as follows, the same letter in each case serving to identify the same product in both tables.

TABLE III

Calculated weight-percentages of enamel compositions

Enamel	A	B	C	D	E
PbO	52.9	50.8	52.9	57.4	47.1
B_2O_3	11.5	11.0	7.7	4.2	20.3
Fe_2O_3	17.6	16.8	13.6	10.3	14.4
Al_2O_3	6.7	6.4	6.7	7.2	6.0
SiO_2	11.3	7.5	11.4	12.2	7.0
CoO	-----	1.8	1.9	2.1	1.7
NiO	-----	1.8	1.9	2.1	1.7
Cr_2O_3	-----	1.9	2.0	2.2	1.8
P_2O_5	-----	2.0	2.1	2.3	-----

These percentages are by weight, based on the total weight of the enamel.

My improved vitreous enamels of the foregoing compositions are prepared in the usual manner by thoroughly mixing the constituents comprising the batch, and then melting the batch in any suitable furnace until a glass of uniform fluidity and sufficiently low viscosity to permit pouring is secured. The melting temperature required to secure the homogeneous melt may vary somewhat but will normally fall within the range 1000° C. to 1300° C. Melting is continued long enough to insure uniformity of melt, and it is especially important that the iron oxide constituent be melted into the glassy phase.

After the meltting is complete the melt is fritted in any suitable manner. Generally it is most convenient to pour the molten glass in a thin stream into water. The granular product thus resulting is then subjected to milling in a ball mill, in accordance with the well-understood procedure in the production of vitreous enamels, in order to reduce its particle size to the desired fineness.

In use, my enamel compositions are incorporated into a slip with water, there being added to this slip various other agents which, in accordance with the usual practice, may constitute dispersing and setting-up agents as well as temporary binders. Such additional agents may include, for example, bentonite, kaolin, ammonium acetate, water soluble gums, ethylene glycol, etc., or any one or more of these agents.

The electrical resistor element or similar piece of electrical equipment, wound upon a suitable ceramic tube or base, to which the enamel is to be applied is then dipped into the slip, or the slip is applied thereto in any other convenient manner. A sufficient quantity of slip containing the enamel should adhere thereto to provide a satisfactory coating completely covering the resistance wire and supporting ceramic base. The electrical element and adhering slip is then dried and placed in a furnace and fired at a temperature in the range 550° C. to 750° C. A temperature within this range is maintained for a sufficient length of time to mature the enamel properly in place on the resistor. The resulting electrical resistor element, or similar piece of electrical equipment, coated with the adhering vitreous insulating enamel, will be found to meet the severe standard test previously described without crazing, cracking, spalling off or breaking. The ability of the enamel to withstand these severe conditions without even developing minute cracks is indeed re-

markable, as no enamel previously available to the industry has exhibited similar ability.

In preparing the enamel compositions it is not necessary in all cases to incorporate either all of the lead oxide or all of the silica ultimately present in the final enamel as fired on the resistor in the original fusion operation, as a part may be added as a mill addition in preparing the slip. For example, as much as 20% to 30% of the total lead oxide content may be incorporated subsequent to fusion and fritting of the enamel by adding it subsequently as a mill addition. Thus, litharge or red lead may be added during milling and, in many cases, I have found it advantageous to add it this way as it permits application of the enamel to the resistance wire without excessive tearing or drawing up of the enamel during firing. This tearing or drawing up of the enamel results in a defect called "swimming" of the winding during firing, i. e., the displacement of the coils of the wire through the action of the enamel. In addition to adding part of the lead oxide in this way as a mill addition it is also frequently desirable to add part of the silica during milling.

As an example of a typical enamel slip wherein part of the lead oxide is added subsequent to fusion and fritting as a mill addition the following is given. Instead of enamel Frit B in Table III any other enamel falling with the scope of my invention as previously set forth may be utilized.

	Parts
Enamel Frit "B," Table III	93
Litharge (PbO)	5
Ethylene glycol	2
Water	50

This composition containing the added lead oxide may be milled for three hours in a porcelain ball mill. The electric resistor is thoroughly covered, both metallic resistance wire and supporting base, with the slip, and upon fusion there results an adherent vitreous enamel of electrical insulating characteristics which will withstand the severe standard test employed in testing the commercial suitability of enameled resistors of this type.

I have tested numerous enameled resistor structures coated with the enamel compositions previously described by heating them to 275° C. and then quenching them in saturated salt water at 0° C. Upon examination I have been unable to detect any evidence of failure. No cracking, spalling off, or crazing of the enamel has occurred. The availability of the enamel withstanding the severe test conditions described makes it possible to manufacture electrical apparatus of this type which may be used in communication equipment and for other purposes without any danger of failure of the electrical element or interruption of its service.

It is obvious that various changes may be made in my invention as above described which will nevertheless come within its scope. While the foregoing enamel compositions constitute examples of preferred enamels, it is obvious that variations in their compositions may be made without surrendering the outstanding advantages of the invention. Thus, the exact compounds used as the source of the oxidic constituents in the vitreous enamels may be varied, and suitable cheap and available sources may be selected. The melting procedure employed may be varied considerably provided homogeneity and thorough melting and fusion of the ferric oxide constituent is secured. It is accordingly my intention that the scope of my invention is to be construed in accordance with the appended claims.

I claim:

1. A vitreous enamel composition suitable for use in enameling electrical resistors which comprises: lead oxide in amounts ranging from 45–65%; silica in amounts ranging from 4–15%; boric oxide in amounts ranging from 4–20%; alumina in amounts ranging from 3–9%; and ferric oxide in amounts ranging from 9–20%, said percentages being by weight based on the total weight of said vitreous enamel.

2. A vitreous enamel composition suitable for use in enameling electrical resistors which comprises: lead oxide in amounts ranging from 45–65%; silica in amounts ranging from 4–15%; alumina in amounts ranging from 3–9%; boric oxide in amounts ranging from 4–20%; ferric oxide in amounts ranging from 9–20%; nickel oxide in amounts ranging from 1–4%, said percentages being by weight based on the total weight of said vitreous enamel.

3. A vitreous enamel composition suitable for use in enameling electrical resistors which comprises: lead oxide in amounts ranging from 45–65%; silica in amounts ranging from 4–15%; alumina in amounts ranging from 3–9%; boric oxide in amounts ranging from 4–20%; ferric oxide in amounts ranging from 9–20%; and cobalt oxide in amounts ranging from 1–5%; said percentages being by weight based on the total weight of said vitreous enamel.

4. A vitreous enamel composition suitable for use in enameling electrical resistors which comprises: lead oxide in amounts ranging from 45–65%; silica in amounts ranging from 4–15%; alumina in amounts ranging from 3–9%; boric oxide in amounts ranging from 4–20%; ferric oxide in amounts ranging from 9–20%; and an oxide of phosphorous in amounts ranging from 1–4%; said percentages being by weight based on the total weight of said vitreous enamel.

5. A vitreous enamel composition suitable for use in enameling electrical resistors which comprises: lead oxide in amounts ranging from 45–65%; silica oxide in amounts ranging from 4–15%; alumina in amounts ranging from 3–9%; boric oxide in amounts ranging from 4–20%; ferric oxide in amounts ranging from 9–20%; cobalt oxide in amounts ranging from 1–5%, nickel oxide in amounts ranging from 1–5%; and chromic oxide in amounts ranging from 1–5%; said percentages being by weight based on the total weight of said vitreous enamel.

ALDEN J. DEYRUP.