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LOW-TEMPERATURE VITREOUS ENAMELS

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The present invention relates to a novel composition adapted for use in the preparation of vitreous coatings for metal articles. More particularly, the invention relates to a composition in the form of a frit, adapted for use as a vitreous enamel in the coating of articles of light metals, such as aluminum, aluminum alloys, magnesium, magnesium alloys, and the like.

Aluminum and aluminum alloys, because of their high strength and light weight, have found increasing use in the manufacture of articles for industrial purposes. Aluminum and aluminum alloys, however, are subject to attack by various substances which is not only detrimental from the standpoint of deterioration of the metal article, but also from the standpoint of contamination of substances brought into contact with the metal article. It has been proposed to apply vitreous enamel coatings to the aluminum or aluminum alloy article in an attempt to protect the metal. There are many problems presented in the application of vitreous coatings on aluminum and aluminum alloys which make most of the presently known vitreous compositions wholly unsuitable as protective and decorative coatings therefor. In the first place, aluminum has a very high coefficient of thermal expansion. The expansion of articles made of aluminum or of aluminum alloys at elevated temperatures thus results in the destruction of vitreous coatings thereon, unless the coating has a coefficient of thermal expansion approaching that of the metal to which it is applied. Most of the presently available enamel compositions have coefficients of thermal expansion much less than that of aluminum and thus are unsuitable, from this standpoint, for use on metal articles made from aluminum or aluminum alloys.

Moreover, ordinary vitreous enamels, particularly those high in P_2O_5 , contain small quantities of water (or hydrogen ion) within the glass structure itself. Because of the reducing action of aluminum at elevated temperatures, hydrogen, as a result, is evolved at the metal-enamel interface as a gas. These gas bubbles destroy adherence of the enamel to the metal. In addition, most existing vitreous compositions which might be suitable for coating aluminum and aluminum alloys from the standpoint of chemical resistivity and water-insolubility, must be fired at relatively high temperatures. Pure aluminum melts at about 1200° F. and aluminum articles become deformed and lose tensile strength at temperatures well below this temperature. In addition, certain aluminum alloys are deleteriously affected at temperatures of about 1000° F. Thus a vitreous enamel having a relatively low maturing temperature at which the metal is not adversely affected is much to be desired. It has also been

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found that with the use of existing enamels, a laborious procedure of pre-treatment of the metal to be coated, is necessary. For instance, it has previously been necessary to treat the metal article first in an oxidizing bath followed by a pre-firing of the metal article. Some or all of the problems referred to above in connection with aluminum and aluminum alloys may also apply to magnesium and its alloys.

Relatively recently, a composition has been developed primarily as a vitreous coating for light metals including aluminum, with the view of overcoming certain of the above difficulties. This composition, however, is composed primarily of lead oxide and silica with minor amounts of other oxides. Lead oxide, as is well known, is toxic, and this characteristic constitutes a considerable health hazard in commercial production. An important feature of the composition of the present invention is that it does not require lead oxide as a constituent thereof, and, in fact, is preferably free of lead oxide.

It is an object of the present invention to provide a composition available for use as a vitreous enamel in the coating of light metals, wherein the above-mentioned difficulties are overcome.

Another object is to provide a vitreous enamel composition which will not be destroyed when applied to articles of light metals, such as aluminum, aluminum alloys, magnesium, magnesium alloys, and the like, when the article is subjected to high temperature.

Still another object is to provide a composition available for use as a vitreous coating for light metals which may be fired at temperatures lower than existing coatings for light metals.

Still another object is to provide a composition which when applied as a vitreous coating to articles of light metals, particularly of aluminum or aluminum alloys, does not result in the formation of gas bubbles at the enamel-metal interface resulting in loss of adherence.

A further object is to provide a composition available for use as a vitreous coating for light metals, such as aluminum, aluminum alloys, magnesium, magnesium alloys, and the like, which permits the simplification of the pre-treatment of the metal article and does away with the cumbersome pre-treatment procedures encountered with the use of prior enameling compositions.

A further object is to provide a composition available for use as a vitreous coating for light metals which does not require lead oxide as a constituent thereof.

A further object is to provide a composition available for use as a vitreous coating for light metals such as aluminum, aluminum alloys, magnesium, magnesium alloys, and the like, having

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the above-described novel properties and also possessing high mechanical adherence to the metal and chemical resistivity.

Further objects will become apparent from a consideration of the following specification and claims.

The novel composition of the present invention, in the form of a frit, comprises between about 5 and about 15 mol percent of Li_2O , between about 15 and about 33 mol percent of Na_2O , between about 3 and about 12 mol percent of an easily reducible oxide selected from the group consisting of CuO , CoO , CdO , and NiO , between about 15 and about 23 mol percent of Al_2O_3 , between about 20 and about 32 mol percent of P_2O_5 , from 0 to about 15 mol percent of B_2O_3 and fluorine in an amount equivalent to between about 2 and about 15 mol percent of Na_2F_2 ; the sum of the mols of B_2O_3 and Al_2O_3 divided by the mols of P_2O_5 providing a ratio of between about .6 and about 1.6 and the sum of the mols of B_2O_3 and of Al_2O_3 and of P_2O_5 divided by the sum of the mols of Li_2O and Na_2O and of the said easily reducible oxide providing a ratio between about 1 and about 1.5.

The above analysis is not intended to exclude small amounts of other reactible oxides which may be included for various purposes. For instance, a small amount of K_2O may be present in the composition. If K_2O is present, it will be in excess of 5 mol percent, more generally not in excess of 2 mol percent of the composition. Likewise, a small amount of the alkaline earth oxides, zinc oxide or antimony trioxide, may be present. Of the alkaline earth oxides, BaO is more favorable from the standpoint of favoring fusibility. Zinc oxide favors chemical resistivity. If such oxides are present, they will not be in excess of 5 mol percent, and more generally not in excess of 2 mol percent. The preferred compositions of the present invention will be substantially free of K_2O , alkaline earth oxides, ZnO , or Sb_2O_3 , consisting essentially of the oxides set forth in the foregoing paragraph. However, as will be discussed more in detail hereinafter, conventional coloring and opacifying compounds may be added to the composition of the invention in accordance with known practice.

The above-described composition has been found to possess many unusual characteristics, making it especially useful as a vitreous enamel composition for articles made of aluminum or aluminum alloys. In the first place, the composition in the form of a vitrified coating possesses a coefficient of thermal expansion approaching that of aluminum. Thus, when articles made of aluminum or of aluminum alloys are subjected to elevated temperatures, there is no danger of the coating becoming cracked or crazed or otherwise destroyed. In addition, it has been found that with the composition of the present invention, there is no formation of gas bubbles at the enamel-metal interface which would result in the loss of adherence between the enamel coating and the metal. This is believed to be due to the fact that the easily reducible oxide of the type mentioned is more easily reduced by the aluminum in the article than is water. Thus, instead of reducing the water (or hydrogen ion) in the vitreous coating to gaseous hydrogen, the said easily reducible oxide becomes reduced by the aluminum to the elemental metal form, and this metal is deposited at an enamel-metal interface inhibiting further

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reaction. It has also been found that with the composition of the present invention, the cumbersome pre-treatment procedure of the metal article to be coated is not required. Thus, in most cases, all that is needed by way of pre-treatment of the metal article is normal removal of grease and other dirt from the surface as by the use of common soaps or detergents, although it is preferred practice also to slightly etch the surface with the help of alkaline or acid solutions. Another important feature of the compositions of the present invention is that they may be fired at temperatures as low as 900°F ., in other words, they have maturing temperatures as low as 900°F . As stated previously, the compositions of the present invention do not require lead oxide as a constituent thereof. This freedom from lead oxide thus eliminates the health hazard encountered previously in cases where lead oxide was used. The compositions of the present invention are also characterized by good mechanical adherence to the metal and chemical resistivity. The properties of adherence, resistivity, and low maturing temperature are, of course, somewhat dependent upon the chemical compositions selected. However, the compositions having the preferred analysis as set forth below exhibit excellent mechanical adherence.

Referring further to the composition of the present invention, it has been found that if the Li_2O is present in an amount less than about 5 mol percent, the coating is too soluble for most purposes and requires a relatively high firing temperature; and if the Li_2O is present in an amount higher than about 15 percent, the coating must also be fired at relatively high temperatures. With respect to the Na_2O , if the amount thereof is outside the above-recited range, the coating has been found to require relatively high firing temperatures. In order to provide the elimination of gas bubbles at the enamel-metal interface, it has been found that the easily reducible oxide of the type set forth above must be present in an amount of at least about 3 mol percent. However, if the amount thereof is higher than about 12 mol percent, the composition requires excessively high firing temperatures. With respect to the Al_2O_3 and the P_2O_5 , it has been found that if these materials are not within the ranges set forth above, the composition is too soluble for most practical purposes or requires excessively high firing temperatures. With respect to the B_2O_3 , it has been found that if this material is present in an amount greater than about 15 mol percent, the coating is too soluble for most practical purposes and becomes excessively hygroscopic, and the frit tends to hydrate upon water quenching. However, amounts less than about 15 mol percent of B_2O_3 , for example, from about 2 to about 15 mol percent, preferably from about 6 to 12 mol percent, are advantageously present, as the presence of the B_2O_3 lowers the firing temperature of the composition. The above-described oxide proportions thus provide proper chemical resistivity and insolubility coupled with reasonably low firing temperatures. The preferred compositions of the present invention will comprise between about 8 and about 13 mol percent of Li_2O , between about 25 and about 30 mol percent of Na_2O , between about 4 and about 6 mol percent of the easily reducible oxide, between about 18 and about 32 mol percent of Al_2O_3 , between about 24 and about 28 mol percent of

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P_2O_5 , between about 2 and about 12 mol percent of B_2O_3 , and fluorine in the amount stated above; and will have a ratio of the sum of mols of B_2O_3 and Al_2O_3 divided by the mols of P_2O_5 of between about 0.8 and about 1.2, and a ratio of the sum of mols of B_2O_3 and of Al_2O_3 and of P_2O_5 divided by the sum of mols of Li_2O and of Na_2O and of easily reducible oxide of between about 1.2 and about 1.4.

Referring to the easily reducible oxide mentioned above, it may be selected from the group consisting of CuO , CoO , NiO , and CdO . Mixture of two or more of these oxides may be employed if desired. All these oxides are di-valent and are more easily reduced by aluminum at elevated temperatures than is water; of the easily reducible oxides, CuO , CoO , and NiO are preferred from the standpoint of ease of reduction, and of these, CuO is most easily reducible and thus most advantageous for use, with CoO of second preference. The easily reducible oxide may impart a characteristic color to the resulting enamel coating. Thus CuO will impart a blue-green color to the coating; CoO will impart a blue color, and NiO will impart a brown color, while CdO imparts no color to the coating. For many purposes, these colored effects are not disadvantageous, however, if different colors are desired they may be provided by the use of conventional coloring agents of the type discussed hereinafter.

The composition, in the form of a frit, having the above-described chemical composition, may be prepared in accordance with conventional practice. As is well-known, in preparing the frit, compounds ultimately providing the desired oxide analysis, in the present case, providing the above-described oxide analysis—are mixed together in fine particle size and melted, and the molten mass quickly cooled, as by water-quenching, and dried. With respect to the compounds employed to provide the above chemical analysis, such compounds are well-known in the art and the provision of the above-described chemical analysis will present no problem to those skilled in the vitreous enamel art. Thus, the Li_2O may be provided, for example, by lithium carbonate, tribasic lithium phosphate, lithium nitrate, and the like; the Na_2O may be provided for example, by sodium carbonates, for instance, soda ash, sodium carbonate monohydrate, and the like, phosphates, for instance tetrasodium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate, and the like, sodium nitrate, borates, for instance, borax, and the like; the easily reducible oxides may be provided, for example, by carbonates of the corresponding metal, or the free oxides themselves may be used; the Al_2O_3 may be provided, for example, by aluminum meta- or ortho-phosphate, aluminum hydroxide, or the free aluminum oxide itself may be used; the P_2O_5 may be provided, for example, by the various phosphates such as the sodium phosphates, for instance those mentioned above, ammonium phosphates, for instance monoammonium phosphate, dibasic ammonium phosphate, and the like, tribasic lithium phosphate, the aluminum phosphates, for instance those mentioned above, and the like; the B_2O_3 may be provided, for example, by borates, such as sodium borates, for instance borax, boric acid, and the like; the fluorine may be provided by any of the alkali or alkaline earth metal fluorides such as sodium fluoride, lithium fluoride, calcium fluoride, barium fluoride, and the like, aluminum fluoride, and more complex fluorides, for in-

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stance, cryolite, and the like. It will be understood, of course, that during melting in the preparation of the frit, a certain amount of fluorine is lost due to volatilization, the exact amount depending upon the fritting procedure followed. The amount of the source of fluorine will, therefore, be selected to provide a fluorine content in the frit as specified above. One compound may provide some or all of a plurality of the above-mentioned oxides, for example, sodium phosphate may be relied upon to provide Na_2O and P_2O_5 . In any event, the compounds will be selected in accordance with well-known practice to provide the proper chemical analysis and in the event such compound contains the constituent not desired in the ultimate frit, such constituent will be of a volatile nature so that it may be removed during the heating and melting of the mixture. For example, where carbonates are employed, carbon dioxide is liberated and where ammonium compounds, such as ammonium phosphate, are employed, the ammonia is liberated.

The materials, in fine particle size, providing the desired chemical analysis upon melting thereof, are mixed together in accordance with common practice and heated to an elevated temperature to provide a molten, pourable mass. With the compositions of the present invention, temperatures in the neighborhood of from about 1800 to about 2000° F. will be required to provide the molten mass. The molten mass is then quickly chilled such as by pouring it into a water bath, and such quick chilling causes the glass-like mass to fracture into small pieces. These small pieces are recovered and dried to provide the frit having the chemical analysis as described above.

The resulting frit may be too coarse for direct use as an enameling composition and may, therefore, be ground to the desired size in accordance with well-known practice. As stated, the composition of the invention may have mixed therein an opacifying agent and the opacifying agent may, in accordance with known practice, be incorporated with the frit during milling. This insures thorough distribution of the opacifier throughout the composition. Opacifiers are well-known and are essentially materials which, in relation to the remainder of the composition, are refractory and which thus do not fuse and dissolve in the composition during firing thereof. They thus remain suspended and dispersed throughout the coating in the form of fine particles imparting opacity to the coating. Examples of opacifiers are zirconium oxide, titanium oxide, other high melting compounds of zirconium and titanium, and of antimony, and the like.

Coloring agents may also be added to the composition, if desired, in accordance with known practice, and these may also be added to the composition during milling thereof. The coloring agents employed may be inert pigments or may be solution colorants. Examples of coloring agents are the various high melting colored cadmium salts, cobalt salts, and the like.

Other additives of the type normally incorporated in vitreous enameling compositions may be added to the composition of the invention. For example, it is normally the practice to incorporate a suspending agent in the composition, usually during milling of the frit. A particularly advantageous suspending agent for use with the present product is sodium silicate, and this may be added either as a solid or as a solution in water.

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Similarly, an electrolyte salt is also normally added to the composition. Such salt flocculates the composition when water is added thereto to provide the slip, and thus serves as a control on the viscosity of the slip. Examples of such salts are the water-soluble, particularly the alkali metal, chlorides, nitrates, phosphates, and the like.

The resulting finely ground mixture, before application as an enamel, will have incorporated therewith a liquid vehicle, most generally water, to impart fluid-flow characteristic to the material, and thus to provide the slurry or slip which is applied to the metal articles. In accordance with common practice, some or all of the water may be added at the mill. Some or all of the above-described additives which are water-soluble may be mixed with the water, and in this way incorporated in the enamel. For instance, the suspending agent and/or the electrolyte salt may be added to the composition as an aqueous solution. In this regard, sodium silicate, either added during milling or subsequently, such as in aqueous solution, functions as a binder imparting strength to the coating until it is fired.

In applying the coating composition to the articles of aluminum or aluminum alloys, the metal articles are previously cleaned of grease and other foreign matter, using soaps and/or detergents and water, and preferably also with the aid of an alkali or acid bath. The composition in the form of a fluid suspension or slurry, termed the slip, is then applied to the cleaned metal article as by spraying, brushing, and the like. The coating is then fired, preferably after excess surface water has evaporated, to cause the coating to fuse and to vitrify into a continuous glassy coating. The firing of the coating follows well known procedures, however, as stated, an important feature of the compositions of the present invention is their ability to be fired at temperatures as low as about 900° F. It will be understood, however, that temperatures above 900° F. may be employed, if desired, although temperatures much in excess of about 1000° F. will generally not be employed for reasons set forth previously.

Two or more coats of the enamel may be, and preferably are, applied. This may be accomplished by following the same procedure each time. For instance, after the first coating has been applied and fired as described, a second coating may be applied and fired in the same manner. In the event only one coating is to be applied, it is preferable to coat the metal surface with a solution of sodium silicate, such as a 5% solution, prior to the application of the slip. This procedure provides an enamel of good surface texture and adherence, free of surface pits which may be associated with the first coating. A top coating of another type of enamel may be applied to a ground or base coat of the enamel of the present invention. For instance, the composition of the present invention, because of its high adherence to aluminum and aluminum alloys may serve as a base coating on which may be applied a second, or "cover" coating which may be of conventional composition.

The preparation of the compositions of the present invention may be readily understood from a consideration of the following specific examples which are given for the purpose of illustration only and are not intended to limit the scope of the invention in any way.

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EXAMPLE I

The following materials, all of which were of a particle size less than 30 mesh, are mixed in the indicated amounts:

	Parts by weight
Lithium carbonate	6.6
Sodium fluoride	7.5
Sodium carbonate monohydrate	22.2
Alumina	9.5
Boric acid	11.5
Aluminum metaphosphate	49.1
Black copper oxide	7.1

These materials are thoroughly mixed in a fire clay crucible and the mixture smelted in a gas-fired pot furnace. Since the copper oxide is sensitive to reduction an oxidizing atmosphere is maintained in the furnace. At a furnace temperature of about 1800° F., the mass completely melts down to a fluid blue-green glass. This takes about 30 to 40 minutes.

The molten mass is then water quenched in accordance with normal practice, and the resulting frit is dried. The frit has an oxide analysis as follows:

	Per cent by weight
Li ₂ O	2.9
Na ₂ O	11.8
NaF	8.0
Al ₂ O ₃	20.3
B ₂ O ₃	6.9
P ₂ O ₅	42.5
CuO	7.6

The frit is prepared as an enamel by mixing in a porcelain jar mill, per 100 parts, by weight, of frit, 2 parts of sodium silicate, .25 part potassium chloride, and 40 parts of water. This mixture is ground in the mill until the residue on a 200 mesh screen is less than 2 grams per 100 cc. of slip. At this point the slip is suitable for application as by spraying, dipping, and the like.

The aluminum panel to be enameled is prepared by washing with soap and water to remove all traces of grease and other foreign matter. After drying the washed panel it is sprayed with the slip to provide about 25 ounces of enamel (dry) to the square foot. As soon as the surface water disappears, the piece is fired at a temperature of 900° F. for five minutes. Higher temperatures may be used in which case the firing time is reduced. For example, at 950° F. the firing time is about 3½ minutes, and at 1000° F. the firing time is about 2½ minutes.

In accordance with preferred practice, a second coat is applied following the same procedure as used in applying the first coat. The resulting enamel is free of surface defects and possesses a high gloss and a pleasing blue-green color.

EXAMPLE II

A mixture is prepared consisting of:

	Parts by weight
Lithium carbonate	7.4
Sodium fluoride	8.4
Sodium carbonate	21.2
Boric acid	20.6
Alumina	12.8
Aluminum metaphosphate	44.0
Titania	5.0
Cobalt oxide	8.1

This mixture is melted and prepared into a frit

following the procedure of Example I. The resulting frit had the following analysis:

	Per cent by weight
Li ₂ O	2.8
Na ₂ O	11.8
NaF	8.0
Al ₂ O ₃	20.3
B ₂ O ₃	11.1
P ₂ O ₅	34.0
CoO	7.2
TiO ₂	4.8

When ground and prepared as a slip following the procedure of Example I, the slip is applied to an aluminum panel and fired at 980° F. for 5 minutes. Two applications are made. The resulting enamel is a semi-opaque cobalt blue.

A wide variety of composition may be prepared following the same general procedure outlined in Example I. Thus by way of further examples, the following compositions are given in which the proportions of the various oxides in the frit are set forth as percent by weight:

Table I

Example	III	IV	V	VI	VII	VIII	IX	X	XI
Li ₂ O	3.6	3.5	2.7	3.3	3.4	2.9	2.7	2.9	2.96
Na ₂ O	13.5	13.1	10.9	14.2	14.9	11.9	11.3	11.9	7.87
NaF	8.2	7.8	7.4	8.1	8.5	8.1	7.7	8.1	14.56
Al ₂ O ₃	20.7	19.9	18.7	20.6	21.5	20.4	19.4	20.4	21.03
B ₂ O ₃	7.0	6.8	6.4	7.0	11.8	6.9	6.6	7.0	2.09
P ₂ O ₅	43.1	41.5	46.9	42.9	35.9	42.6	40.6	42.6	43.91
CuO	3.9	3.7	7.0	3.9	4.0				7.87
CoO						7.2			
CdO							11.7		
NiO								7.1	
TiO ₂		3.7							

Considerable modification is possible in the selection of the ingredients, as well as in proportions thereof, in the preparation of the composition of the present invention without departing from the scope of the present invention.

I claim:

1. A composition in the form of a frit, available for use as a vitreous enamel composition comprising:

Li₂O—between about 5 and about 15 mol percent
Na₂O—between about 15 and about 33 mol percent

an easily reducible oxide selected from the group consisting of

CuO, CoO, NiO, and CdO—between about 3 and about 12 mol percent

Al₂O₃—between about 15 and about 23 mol percent

P₂O₅—between about 20 and about 32 mol percent

and fluorine in an amount equivalent to between about 2 and about 15 mol percent of Na₂F₂; the sum of the mols of any B₂O₃ and of Al₂O₃ divided by the mols of P₂O₅ providing a ratio between about 0.6 and about 1.6, and the sum of the mols of any B₂O₃ and of Al₂O₃ and of P₂O₅ divided by the sum of the mols of Li₂O and of Na₂O and of the said easily reducible oxide providing a ratio between about 1 and about 1.5.

2. The product of claim 1 wherein said easily reducible oxide comprises CuO

3. The product of claim 1 wherein said easily reducible oxide comprises CoO.

4. The product of claim 1 wherein said easily reducible oxide comprises NiO.

5. A composition in the form of a frit, avail-

able for use as a vitreous enamel composition comprising:

Li₂O—between about 8 and about 13 mol percent
Na₂O—between about 25 and about 30 mol percent

an easily reducible oxide selected from the group consisting of

CuO, CoO, NiO, and CdO—between about 4 and about 6 mol percent

Al₂O₃—between about 18 and about 20 mol percent

P₂O₅—between about 24 and about 28 mol percent

B₂O₃—between about 2 and about 12 mol percent

and fluorine in an amount equivalent to between about 2 and about 15 mol percent of Na₂F₂; the sum of the mols of B₂O₃ and of Al₂O₃ divided by the mols of P₂O₅ providing a ratio between about 0.8 and about 1.2, and the sum of the mols of B₂O₃ and of Al₂O₃ and of P₂O₅ divided by the sum of the mols of Li₂O and of Na₂O and of the said easily reducible oxide providing a ratio between about 1.2 and about 1.4.

6. The product of claim 5 wherein said easily reducible oxide comprises CuO.

7. The product of claim 5 wherein said easily reducible oxide comprises CoO.

8. The product of claim 5 wherein said easily reducible oxide comprises NiO.

9. A composition in the form of a frit, available for use as a vitreous enamel composition comprising:

Li₂O—between about 5 and about 15 mol percent
Na₂O—between about 15 and about 33 mol percent

an easily reducible oxide selected from the group consisting of

CuO, CoO, NiO, and CdO—between about 3 and about 12 mol percent

Al₂O₃—between about 15 and about 23 mol percent

P₂O₅—between about 20 and about 32 mol percent

B₂O₃—up to about 15 mol percent

and fluorine in an amount equivalent to between about 2 and about 15 mol percent of Na₂F₂; the sum of the mols of B₂O₃ and of Al₂O₃ divided by the mols of P₂O₅ providing a ratio between about 0.6 and about 1.6, and the sum of the mols of B₂O₃ and of Al₂O₃ and of P₂O₅ divided by the sum of the mols of Li₂O and of Na₂O and of the said easily reducible oxide providing a ratio between about 1 and about 1.5.

10. The product of claim 9 wherein said easily reducible oxide comprises CuO.

11. The product of claim 9 wherein said easily reducible oxide comprises CoO.

12. The product of claim 9 wherein said easily reducible oxide comprises NiO.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,436,825	Prior	Mar. 2, 1948

FOREIGN PATENTS

Number	Country	Date
30,168	Austria	1906