

1

2,889,238

COATING FOR CLEANING AND PROTECTING METALS

John V. Long, San Diego, and John V. Furth, La Jolla, Calif., assignors to Solar Aircraft Company, San Diego, Calif., a corporation of California

No Drawing. Application July 13, 1954
Serial No. 443,172

22 Claims. (Cl. 117—103)

This invention relates generally to protective coatings and more specifically to novel means and methods for protecting the surfaces of certain metals and metallic alloys from oxidation when subjected to high temperatures as during heat treat cycles, welding operations, brazing, metallic coating, and the like for cleaning said surfaces of pre-existing oxides or other impurities thereon, and to novel methods of flow coating basis metals with protective metallic coating layers.

An important utility of the present invention is in the heat treatment of these metals and alloys during fabrication. It is well known that when certain metals and alloys are being machined or formed from the rough state to the finished article, they are work-hardened and therefore must be subjected to an annealing heat treatment. Standard annealing procedure involves heating the article in air; and as a result of and during this step, oxygen attacks the exposed surfaces and forms a tenacious oxide film thereon. Also, in accordance with standard procedure, this oxide film must be removed and requires such time-consuming and relatively costly post-heat treat cleaning steps as pickling, sandblasting, a combination of caustic and acid cleaning and/or various other known procedures and combinations of procedures.

Efforts have been made in dealing with certain industrial metals to eliminate the necessity for these oxide removal steps by coating the metals with various compositions before subjecting them to heat treatment and thus preventing formation of oxides. Such compositions as have been proposed provide only partial solutions to the problem for various reasons. For the most part, only imperfect oxidation prevention is attained and/or additional steps are required to effect removal of the protective coating. Also, these prior art coatings usually leave the metal surface in substantially the same condition as when applied, that is, pre-existing oxides on such surfaces are not removed by the coating.

The present invention may also be utilized to great advantage as a flux in welding, brazing, metallic coating, surface cleaning and protection, and operations where removal of flux residues and slag formations have long been a problem, as hereinafter more fully described.

In its broadest aspects, the invention contemplates novel amorphous or vitreous glass-like coatings characterized by co-efficients of expansion different than the metal or alloy to which applied and high fluxing action. These coatings, because of their unique characteristics adhere to and completely protect a metallic surface from oxidation at temperatures above which oxidation usually takes place, for example about 600° F. Below these temperatures the coatings completely spall off and, in so doing, carry with them any oxide film which may have been present on the metal before coating, leaving the surface chemically clean and bright.

The fundamental object of the present invention is to provide novel coating compositions for protecting and cleaning metallic surfaces subjected to high temperature.

Another important object is the provision of improved

2

coating compositions which adhere to metallic surfaces at temperatures in excess of approximately 600° F. and do not adhere at room temperatures.

Still another object of this invention is the provision of novel compositions of matter which form an impervious coating on metallic surfaces at temperatures exceeding approximately 600° F., protecting said surfaces from oxidation, and removing existing oxides therefrom.

A further object is to provide means and methods for the removal of oxide films from metallic surfaces.

Still another object is to provide an improved method for heat treating metals which eliminates the need for the customary expensive and time consuming post-heat treat cleaning procedures such as pickling, hydride cleaning, sandblasting, etc.

A more specific object is the provision of novel borate or borosilicate compositions which form vitreous glass coatings when fired on metallic surfaces, which coatings are characterized by strong fluxing action, thermal expansion co-efficient different from the metal or alloy to which applied, the ability to adhere at temperatures in excess of approximately 600° F. and protect said surfaces from oxidation and to literally "pop off" spontaneously at lower temperatures, removing themselves as well as impurities pre-existing on said surfaces.

Still another object is a novel composition of matter for the protection of metallic billets during soaking operations which composition of matter when applied to said billet will prevent a loss of metal through oxidation.

A further object is provision of a novel composition of matter which is useful in protecting metals and alloys against oxidation during rolling, drawing, and/or forming operations.

A still further object is the provision of improved fluxing compositions for protecting and fluxing metal surfaces during welding and brazing operations which compositions require no subsequent cleaning or removal processes.

Another important object of the invention is to provide novel compositions for use as protective vehicles in metallic coating processes wherein a basis metal is coated with a molten coating metal or alloy.

Another object is the provision of fluxing and coating compositions as characterized above certain formulations of which utilize inexpensive occurring minerals.

These and other objects and the advantages of this invention as well as the manner in which it may be performed to accomplish these objects will be apparent from the following description and subjoined claims.

As previously stated, the general inventive concept disclosed herein is susceptible of various and diverse applications, the more important of which will now be explained before proceeding to a description of the general type and specific examples of compositions embraced thereby. It is pointed out therefore, that in the ensuing description, the compositions referred to are those contemplated by the invention and hereinafter described.

HEAT TREATING AND SURFACE CLEANING

When applied to heat treating of metals, the compositions of the invention are formed into a slip and applied to the surface of the metal as a coating by spraying, painting, dipping, or other suitable and convenient method. Having been applied to the surface of the metal, the coating is dried and the heat treat process is carried out in the normal manner for the particular metal involved. During heating, the slip forms a continuous, impervious, glass-like coating which not only protects the metal from oxidation but also absorbs and holds in suspension any oxides or like impurities present on the surface. Compositions according to the invention soften and flow starting at approximately 1300° F. and provide

3

complete protection during heat treating at temperatures up to in excess of 2000° F.

Upon completion of the heating step, the metal is allowed to cool naturally or is forced cooled by quenching, for example, in water or oil, by use of cooling air blasts or by whatever means and at whatever rate is necessary in the particular heat treat process being used. Regardless of the manner or rate of cooling, the coating continues to protect the metal until the temperature is reduced to well below its oxidation range and the coating then will completely and spontaneously spall off leaving the surface of the metal chemically clean and bright, entirely free of surface impurities.

It will be understood that the same procedure may be utilized to clean the surface of metals without regard to heat treatment thereof.

Furthermore, the coating compositions described herein may be applied to protect metallic billets during soaking operations, thus preventing loss of metal through oxidation, and to protect metals and alloys against oxidation during rolling, drawing, and/or forming operations in manners that will be apparent to those skilled in the art.

The precise manner in which the coating spalls off depends on its specific composition as hereinafter explained, as well as the nature of the basis metal and cooling. In some cases, checking or granulation of the coating initiates in a localized area and rapidly spreads until the entire coating disintegrates into unadhered particles while different compositions and conditions result in the coatings literally "popping off" in sheets. In any case, the removal is spontaneous and complete, occurs below oxidizing temperatures and leaves the surface of the metal chemically clean and bright.

The processes disclosed are effective on a great range of ferrous and many non-ferrous metals and alloys, the non-ferrous alloys being in general those classed as the "super" alloys and including Inconel, N-155, L-605, and others of this series. However, because the glassy phase exhibited by coatings according to our invention solidifies between 1400° F. and 1320° F. during cooling, these coatings are not as satisfactory for use on metals and alloys which go through a crystal transformation stage, which entails expansion, in this temperature range. Such alloys, for example, as 17-22-A, AMS 501, 4130, 410 and 430 appear to experience an appreciable expansion during the cooling cycle and, because the glass has solidified, there is a tendency for it to craze and develop discontinuities, thus allowing some oxidation of the basis material before the non-oxidizing temperature is reached. Further, this crazing of the glass reduces the stress in the glass, thus to a large degree destroying the complete spall which is desirable for optimum automatic removal of the coating.

WELDING AND BRAZING

Another application of our invention is to welding and brazing operations, in which case the compositions may be formed into a slip for use as a flux, in addition to or in lieu of and in the same manner as conventional fluxes. Thus, the slip may be applied directly on the metal surface in the welding area or over regular fluxes, and on either or both sides of the work. During the welding, the composition forms a glassy viscid covering which fluxes oxides from the molten "puddle" and protects it from further oxidation. Upon cooling, whether natural or induced, the coating spalls off as hereinabove described when the temperature falls below the critical or oxidizing temperature range.

METAL FLOW COATING PROCESS

Still another application of the invention is in fusion metal or alloy coating of one metal or alloy upon another as, for example, where the coating metal for example, bronze, silver, chromium-nickel-boron, nickel-manganese, or other metals and alloys which melt in the

4

protective range of the flux, is in granular or powder form and is brought into contact with the surface of the basis metal to be coated and heat applied, causing the coating metal or alloy to fuse and bond on or alloy with the basis metal. In applying the present invention to such coating processes, a satisfactory procedure is to mix the powdered or granulated plating metal into a slip formed of the compositions hereinafter described, and raise the temperature to the level necessary to achieve proper flow of the coating metals or alloys involved. Our novel compositions flux the surface of the basis metal as well as the individual particles of the coating metal or alloy, cleaning and protecting both from oxidation and promoting smooth flow and uniform, cohesive bonding of the coating metal. Upon cooling, the flux compositions spall off as hereinbefore described leaving the basis metal with a protective metallic surface coating.

SPALL OFF COATING COMPOSITIONS

In general, a coating thickness of .008 inch provides adequate protection, but a thicker coating may be used if necessary or desirable. Spalled coatings may be reused in making up additional coating by adding them in quantities amounting up to 50 percent of fresh materials in the batch.

In general, the glass-like spall-off coating compositions contemplated by the invention comprise a glass composed of a frit of boron oxide (B_2O_3) and an alkaline earth, with an optional content of silica (SiO_2) or calcium fluoride (CaF_2) and with mill additions consisting of a suspension agent and a liquid vehicle. A preferred exemplary composition according to the invention is given below:

Example I

Barium oxide (BaO) and boric anhydride (B_2O_3) are mixed in a molar ratio of 1:3, that is, 152 parts BaO to 210 parts B_2O_3 , by weight, with up to one mol (60 parts by weight) of silica (SiO_2). Preferably these ingredients are in granulated condition and fine enough to pass through a 200 mesh screen. The mixture is smelted at approximately 2300° F. until the ingredients combine to form a clear, liquid glass. Substantially this same glass may be obtained by using barium carbonate ($BaCO_3$) and boric acid (H_3BO_3) in a molar ratio of 1:6, that is 197 parts $BaCO_3$ to 372 parts H_3BO_3 in place of the barium oxide and boric anhydride, respectively. For a lower melting point composition, the silica may be replaced with calcium fluoride as hereinafter explained.

The melt then is fritted in cold water or formed into flake by squeezing through water cooled rolls. Fifty parts by weight of the frit thus obtained is then mixed with 30 parts of fused alumina (Al_2O_3), 20 parts of clay, and 50-60 parts of water until thorough mixing is achieved. We prefer to use a medium set clay in our processes. The resulting product is one form of the basic slip contemplated by the invention, ready for the various applications outlined hereinabove. This particular exemplary slip is especially useful where temperatures to be encountered are in excess of 1600° F. and of greater than 15 minutes duration.

If it is necessary or desirable to apply the slip a considerable time prior to heat treatment, or if the parts to which it is applied will be subjected to considerable rough handling, a small amount, for example approximately 3 percent by weight, of ammonium chloride (NH_4Cl) may be added during mixing to increase bisque strength. During heating, the ammonium chloride will volatilize with no deleterious effects.

The various ingredients of the preferred slip have the following apparent functions:

In protecting the coated metal, the barium oxide acts as a flux and lowers the melting temperature of the glass while the boron oxide is highly effective as the cleaning agent and forms the body of the protective coat. The

optional silica content, when used, increases the viscosity of the composition and the alumina increases the refractoriness to resist the heat to which it is subjected. Furthermore, the alumina strengthens the coating so that it will spall as a sheet rather than in small fish scales. The clay is used as a suspending agent and binder, and to prevent tearing. The water serves as a vehicle.

Before describing variations of the preferred composition, it is pointed out that we believe an essential feature of coating compositions according to the present invention is that they produce coatings which have coefficients of expansion different (usually lower) than those of the metals to which they are applied. Furthermore, while the coating glass formed must be sufficiently adherent to provide protection, it must not be so adherent as to result in portions sticking to the metal surface when the coating spalls off. The coating compositions herein disclosed have these unique and necessary qualities. It is believed that this may be due to the absence of sodium in the composition. Sodium, at the temperature involved, appears to react with and etch the metal surface and increases the co-efficient of expansion of the coating so that it tends to adhere to the metal on cooling.

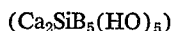
In like manner, alkali salts are not used and calcium fluoride is used only in small quantities as an optional ingredient and alternate for silica. This is because the alkali salts and large proportions of calcium fluoride appear to develop coatings which do not spall.

The preferred composition already described in detail as Example I may be varied by replacing the barium oxide with equimolecular quantities of calcium oxide (CaO) or strontium oxide (SrO). Magnesium oxide (MgO) also may be used, however, only about one-half mol of the barium oxide may be replaced with one-half mol of magnesium oxide. The latter substitute, that is magnesium oxide for a portion of the barium oxide, appears to greatly reduce the co-efficient of expansion of the coating. Therefore, the desirability and extent of such substitution is determined by the metal to be protected.

The molar ratio between barium oxide and boron oxide, given as 1:3, respectively, for the preferred composition, may vary from approximately 1:2 to 1:5. The same ratios appear useful when the other specified alkaline earth oxides are substituted for barium oxide.

At temperatures not substantially above 1600° F., satisfactory frits may be made by substituting calcium fluoride for silica. Up to one mol of calcium fluoride may be used to decrease viscosity and lower the melting point of the bisque. This fritted composition is combined with between 15 and 20 percent clay and a water carrier to provide a satisfactory coat.

We have found that the inexpensive natural mineral colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) and the less well known natural mineral howlite



may be used to advantage in formulating the compositions and carrying out the processes of this invention. These minerals may be utilized primarily as a low cost source of B_2O_3 and CaO, the latter to replace the BaO of the preferred formula. While such minerals form a glass too fluid at high temperature to be used by itself, they give excellent results when smelted with SiO_2 and Al_2O_3 .

Example II

A specific colemanite or howlite type batch in parts by weight is: 100 parts colemanite or howlite mixed with 14 parts SiO_2 and 20 parts Al_2O_3 , the mixture smelted at 2400° F. for from 40 to 45 minutes or until complete degassing is achieved and a clear glass is formed. The smelt is then quenched in any desired manner. The resultant frit, mixed with 20 percent clay, and about 50-60 parts of water to form a slip, is satisfactory for protection at up to 2000° F. for about 15 minutes. If further

protection is desired, a slip of 50 parts of frit, 30 parts SiO_2 and 20 parts clay provides a very refractory coating which gives good protection up to 2000° F. for at least 4 hours.

It should be understood that colemanite and howlite may be used in a wide range with silica and alumina to achieve a satisfactory frit. We have found that one useful mixture prior to smelting contains at least 75 percent colemanite with the silica-alumina weight ratio varying from approximately 1:1.5 to 1:2.

Example III

A satisfactory flux for welding or brazing consists of 80 percent $\text{BaO} \cdot 3\text{B}_2\text{O}_3 \cdot \text{SiO}_2$ frit, as described above under Example I, and 20 percent clay mixed with sufficient water to develop a pasty slip. We have found that approximately 50 parts of solids and approximately 50 parts of water form a paste which can easily be applied yet will not run.

In furnace brazing, the slip may be painted over the braze metal and allowed to dry before the part is put into the furnace. If rapid drying is desired, alcohol, for example, methanol or similar liquid may be substituted for water as the vehicle.

The formula of Example III has proved satisfactory for use with several nickel-manganese and nickel-chromium-boron brazing alloys and has made air brazing possible where formerly special atmospheres were required. This formula also has proved useful with various bronze and silver brazing alloys.

If the brazing alloy is susceptible to considerable oxidation before flowing, it may be desirable to add a small amount of a lower melting flux to secure complete fluxing action. Generally, during the cooling cycle, the flux of our invention removes the additional flux during the spontaneous spalling process.

The formula of Example III may also be used as a front or backup flux in welding and will prove satisfactory if the temperature of the basis metal remains below about 2300° F. At higher temperatures, there may be a tendency for the B_2O_3 to be reduced, permitting the boron to alloy with the basis metal causing brittleness and cracks.

Two variations of our basic formula, particularly useful in metal coating processes are shown in Examples IV and V, herein below. The general procedure is to provide a metal powder of a fineness such that it will pass through a 200 mesh screen, form a slip of said metal powder and the desired frit, clay, and water vehicle, apply the slip to the basis metal, raise the temperature of the basis metal to the flow point of the powdered metal, and hold at the required temperature a sufficient length of time to assure the coating metal has flowed and completely covered the basis metal. During the process, our novel formulas clean the surface to be coated and the coating metal particles, promoting an optimum contact of the two. Our formulas further protect both basis metal and powder granules from further oxidation, and, at the proper time during the cooling cycle, spontaneously spall off, leaving the coating metal in a tightly bonded sheet on the basis metal.

Example IV

When temperatures to be encountered will not exceed 1750° F., we have successfully used a slip composed of about 30 percent powdered metal, about 50 percent $\text{BaO} \cdot 3\text{B}_2\text{O}_3 \cdot \text{SiO}_2$ frit, about 20 percent clay, and approximately 50-60 parts of water to each 100 parts of dry ingredients.

Example V

However, when temperatures are higher than approximately 1750° F., for example in the 2000° F. range, it is desirable to replace approximately 10 percent of the frit with a like amount of fused alumina powder, as hereinbefore discussed.

In general for flow coating, only metals and alloys

which will melt and flow in temperature range where the spall coat retains its protective qualities should be used. The formula of Example IV is particularly satisfactory when coating with bronze and silver powders, while the higher temperature formula (Example V) is desirable when chromium-nickel-boron, nickel-manganese, and like higher temperature powders are used for metal coating. The formula of Example V gives effective protection up to 2200° F.

While our invention has been described and discussed as a glassy coating which results from the application of a slip made from a frit to a metallic surface, it will be understood that a slip made from a dry unreacted mixture of boric anhydride and one of the recited alkaline earth metal compounds may be applied to a surface to be protected and cleaned, and the subsequent heat treat, welding operation, or other application of heat will cause the powdered mixture to melt and flow, forming a cleansing and protecting coat which will spall from the surface during the cooling period, carrying with it pre-existing oxides. We prefer to use a frit for making the slip as above described because of ease in handling, better part coverage, and more consistent results.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. A heat reacted composition of matter consisting essentially from 2 to 5 molar parts of boric anhydride, one-half to one molar part of at least one alkaline earth oxide selected from the group consisting of barium oxide, calcium oxide, strontium oxide, and magnesium oxide, and up to one molar part of a compound selected from the group consisting of silicon dioxide and calcium fluoride.

2. A slip for flow coating a metallic surface with a metal from the group consisting of bronze, silver, chromium-nickel-boron, nickel-manganese, and other metals and alloys which melt between about 1300° F.-2200° F., consisting essentially of about 30 parts by weight of said coating metal in particle form, about 40 parts by weight of the composition of matter defined in claim 1, about 10 parts by weight of fused alumina, about 20 parts by weight of clay, and about 50 parts by weight of water.

3. The method of applying a metal coating to a metallic surface which consists of the steps of applying a layer of the slip defined in claim 2 to said metallic surface and firing the surface at a temperature equivalent to the flow point of said powdered metal or alloy in said slip.

4. The composition of matter defined in claim 1 wherein the alkaline earth oxide content of said mixture consists of one-half to one mol part of barium oxide and up to one-half mol part of magnesium oxide, the mol fractions of barium oxide and magnesium oxide in said alkaline earth oxide content totaling unity.

5. The method of preparing the heat reacted mixture of claim 1 which consists of the steps of combining the said ingredients thereof, smelting them at about 2300° F. until a clear molten glass is formed, and then fritting said molten glass.

6. A welding and brazing flux composition consisting essentially of about 80 parts by weight of a frit of the composition defined in claim 1 and about 20 parts by weight of clay and mixed with sufficient liquid vehicle to form a slip, said liquid vehicle being selected from the group consisting of water and methyl alcohol.

7. A frit consisting essentially of a heat reacted mixture of boric anhydride and at least one alkaline earth oxide selected from the group consisting of barium oxide, calcium oxide, strontium oxide, and magnesium oxide, the molar weight ratio of boric anhydride to alkaline earth oxide in said compound being from 2:1 to 5:1, and up to 1 mole of silica.

8. A slip for fluxing and coating metals consisting essentially of approximately 50 parts by weight of the frit defined in claim 7, approximately 30 parts by weight of fused alumina, a suspension agent and a vehicle.

9. The slip defined in claim 8 including approximately 3% by weight of ammonium chloride.

10. A welding and brazing flux composition consisting essentially of about 80 parts of weight of the frit defined in claim 7, about 20 parts by weight of clay, and mixed with sufficient liquid vehicle to form a slip, said liquid vehicle being selected from the group consisting of water and methyl alcohol.

11. As a novel composition of matter, the smelted and fritted product of a mixture of at least 75 percent by weight of the naturally occurring mineral colemanite, the balance of said mixture consisting essentially of silicon dioxide and alumina in the ratio of approximately 1:1.5 to 1:2.

12. A slip composed of about 80 parts by weight of the composition of matter defined in claim 11, about 20 parts by weight of clay and 50 to 60 parts by weight of water.

13. A slip composed of about 50 parts by weight of the composition of matter defined in claim 11, about 30 parts by weight of silicon dioxide, about 20 parts by weight of clay and about 50 parts by weight of water.

14. A slip comprising as its essential ingredients: a major portion of a frit consisting essentially of boric anhydride and an alkaline earth oxide selected from the group consisting of barium oxide, calcium oxide, strontium oxide, and magnesium oxide, the molar ratio of alkaline earth oxide to boric anhydride being from substantially 1:2 to 1:5, and up to substantially 1 mole of at least one material from the group consisting of silica and calcium fluoride; a minor portion of a suspension agent; and a sufficient amount of a liquid vehicle to form a paste.

15. The slip of claim 14 in which the suspension agent is clay and the liquid vehicle is water.

16. The slip of claim 14 in which there is present substantially 30 parts by weight of fused alumina.

17. The slip of claim 14 in which there is present a minor portion of a powdered metal from the group consisting of bronze, silver, chromium-nickel-boron, nickel-manganese, and other metals and alloys which melt between about 1300° F.-2200° F.

18. The slip of claim 17 wherein there are 50 parts of said frit, 30 parts of said powdered metal, 20 parts of clay as suspension agent, and 50 parts water.

19. The method of applying a metal coating to a surface of a metal member comprising the steps of applying a coating of the slip of claim 17 on a surface of the member; heating the member to a temperature sufficient to cause the powdered metal to flow and for at least a sufficient time to form a glass-like coating on the member; and cooling said member to a temperature to spontaneously spall off from the member said glass-like coating to leave a coating of metal on said member formed from the powdered metal in said slip.

20. The method of heat treating a metal member comprising the steps of applying to a surface of the member a coating of a paste composition comprising as its essential ingredients a major portion of a frit consisting essentially of boric anhydride, and at least one alkaline earth oxide selected from the group consisting of barium oxide, calcium oxide, strontium oxide, and magnesium oxide, the molar ratio of alkaline earth oxide to boric anhydride being from substantially 1:2 to 1:5, and

up to 1 mole of at least one compound from the group consisting of silica and calcium fluoride, a minor portion of a clay, and a sufficient amount of a liquid vehicle to form a paste; heat treating the member at a temperature of at least about 1300° F. for at least a sufficient time to cause a protective glass-like coating to form on the member; and cooling said member to a temperature below about 600° F. to spontaneously spall off from the member said glass-like coating.

21. The method of removing oxide films from iron based, cobalt based, and nickel based alloys and temporarily protecting a surface of said alloys from oxidation during heat treatment comprising the steps of applying to a surface of the member a coating of a slip comprising as its essential ingredients a major portion of a frit consisting essentially of boric anhydride and at least one alkaline earth oxide selected from the group consisting of barium oxide, calcium oxide, strontium oxide, and magnesium oxide, the molar ratio of alkaline earth oxide to boric anhydride being from substantially 1:2 to 1:5, and up to 1 mole of silica, a minor portion of clay, and a sufficient amount of a liquid vehicle to form a paste; heat treating the member at a temperature of at least about 1300° F. for at least a sufficient time

to cause a protective glass-like coating to form on the member; and cooling said member to a temperature below about 600° F. to spontaneously spall off from the member said glass-like coating and remove said oxide film.

22. A heat reacted and fritted composition of matter consisting essentially of from 2 to 5 molar parts of boric anhydride, and one-half to one molar part of at least one alkaline earth oxide selected from the group consisting of barium oxide, calcium oxide, strontium oxide, and magnesium oxide.

References Cited in the file of this patent

UNITED STATES PATENTS

1,856,303	White	May 3, 1932
2,030,390	Navias	Feb. 11, 1936
2,338,165	Caugherty	Jan. 4, 1944
2,393,449	Armistead	Jan. 22, 1946
2,530,217	Bain	Nov. 14, 1950
2,615,817	Stanworth	Oct. 28, 1952

OTHER REFERENCES

Metal Finishing, vol. 50, #10, October 1952, p. 61.