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3,278,324

CORROSION RESISTANT METAL MEMBERS

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Fig. 1.

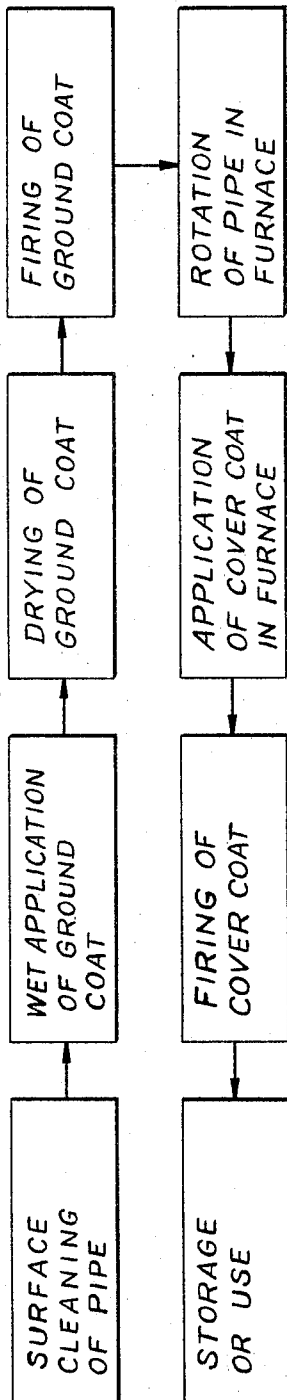


Fig. 2.

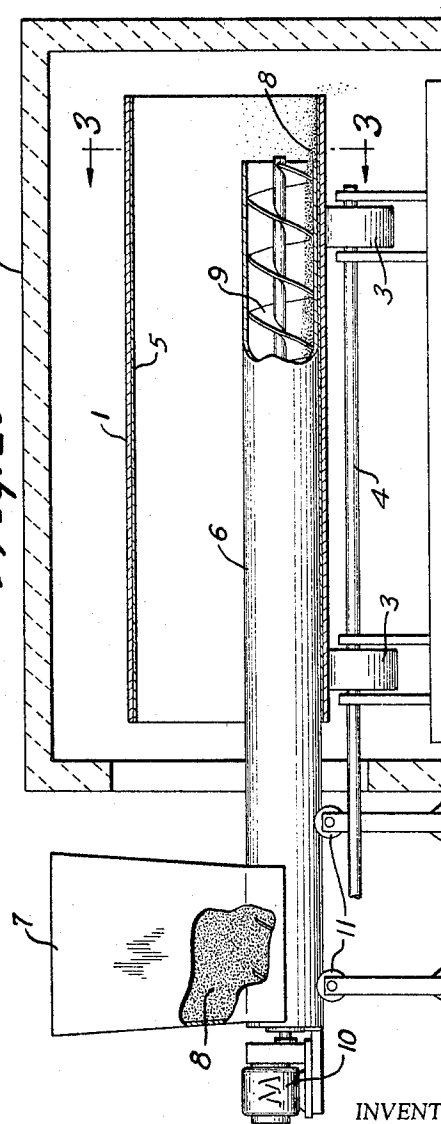
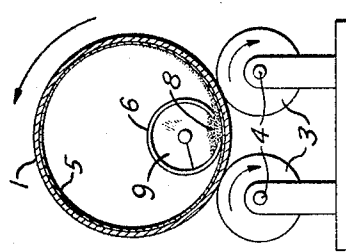


Fig. 3.



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CORROSION RESISTANT METAL MEMBERS

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This invention relates to a corrosion resistant metal member and to a method for lining the metal member, and particularly an internally glass coated tubular article and the method for applying the glass coating to the inner surface thereof.

The pipeline transmission of large volumes of corrosive liquids and gasses has established a substantial market for corrosion resistant pipe. Metal pipe lined with vitreous enamel offers the greatest market potential in this area because of its high corrosion resistance and low flow resistance.

Unfortunately, great difficulty has been experienced in successfully applying a vitreous enamel coating to the inner surface of a length of pipe which is free from defects such as pin holes, bubbles, and abrasions. This difficulty has been most prevalent in the production of glass-lined pipe having a small inner diameter and in pipe of moderate to substantial length. The presence of even a few such defects in a corrosive environment will very quickly destroy the effectiveness of the corrosion resistance of the glass coating.

The objective of research leading to the development of the instant invention was to provide a metal pipe with a defect-free corrosion-resistant glass lining, which could be produced under a commercially competitive process.

In the commonly employed process for glass coating the metal surface of an object, the surface to be coated is thoroughly cleaned, usually by grit or sand blasting. A vitreous enamel ground coat, which acts as a surface sealer and to establish a chemical bond with the metal, is wet sprayed over the surface to be coated. The surface is dried, and the object is placed in a furnace where the dried vitreous enamel is heated to its maturing or fusion temperature. At this stage the vitreous enamel becomes bonded to the metal surface. The object is then permitted to cool. A vitreous enamel cover coat is wet applied to the ground coat surface. The object is then returned to the furnace and is fired. The object is again permitted to cool and additional wet cover coats are applied in a similar manner to the previously coated surfaces, with each cover coating phase requiring a cooling of the object for the wet application and a refiring of the surface to bond it to the previous surface coating.

This process provides a simple, although somewhat expensive, method for coating readily accessible surfaces but produces unacceptable results when the surfaces to be coated are not easily reached by conventional glass coating applicators. The process of the instant invention, however, provides a method wherein only a single firing of the object to be coated is required. As in the commonly used processes, the ground coat of the invention is usually wet applied to the object. The object is then fired to mature the ground coat. When this has been accomplished, the cover coat is applied over the ground coat while the object is maintained at about the ground coat firing temperature. A single cover coat application under this method has been found to be sufficient to provide a smooth, corrosion resistant surface. The elimination of firing and additional cover coat applications has greatly reduced the costs of coatings applied even to readily accessible surfaces.

In coating the internal surfaces of tubular articles, specialized vitreous enamel applicators have been developed. They have taken, in varying designs, the form

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of frit carrying conduits, lances and spray nozzles. All such devices have been found to have at least one major shortcoming. When they are used to apply a cover coat frit powder to a small diameter pipe or pipe of moderate length which has been treated with a vitreous enamel ground coat, portions of the frit depositing device invariably contact and drag along the soft surface of the vitreous enamel ground coat, marring the surface. This is a result of the inability to effectively cantilever and align the frit distributing device in a manner such that the device is maintained completely out of contact with the soft ground coat surface.

In applying frit to small diameter pipe or pipe of moderate length with a conduit, lance or nozzle type applicator, some degree of sag of the applicator has been found to be unavoidable. Some portion of the sagging applicator ultimately comes into frictional contact with the soft surface of the ground coat with a result initial marring of the surface during application of the cover coat and a subsequent marring of the ground coat as the applicator is withdrawn.

The marred surface generally results in the exposure of portions of the inner metal surface of the pipe. The subsequently applied vitreous enamel cover coat which comes into contact with such bare areas generally develops substantial surface defects such as blisters and pits during the firing phase of the cover coat. These surface defects usually result in a rapid deterioration of the pipe adjacent the defective areas when subjected to a corrosive environment.

To overcome this problem, a vitreous or porcelain enamel ground coat has been developed which will mature in the early stages of firing to produce a relatively hard and non-sticky surface at the maturing temperature prior to the application of a glass cover coat composition. In utilizing the ground coat of the invention, one is able to employ a non-cantilevered frit depositing apparatus in applying the cover coat composition to the interior of the pipe and no specialized aligning equipment is required. Since the ground coat matures at an early firing phase and is then in a relatively hard, non-sticky condition and remains in this condition at the maturation temperature and below, the frit applicator may freely contact the ground coat surface without damaging or marring it. The cover coat glass applicator, may, therefore, be inserted into continuous contact with the internal surface of the pipe, actuated to deposit a glass coating composition along substantially the entire length of the pipe and may be withdrawn from the pipe without danger of marring the ground coat surface to an extent such that the subsequently applied cover coat would develop surface defects.

The accompanying drawings illustrate the mode presently contemplated for carrying out the invention.

In the drawings:

FIGURE 1 is a flow diagram showing the steps followed in glass coating a metal object according to the invention;

FIG. 2 is a longitudinal sectional view of a length of pipe at the cover coat station of a furnace showing a glass composition applicator disposed in glass depositing relationship with the inner ground coated surface of the pipe; and

FIG. 3 is a cross-sectional view of the pipe taken on line 3—3 of FIG. 2.

The process of the invention as outlined in the flow diagram of FIGURE 1 is designed to produce a corrosion resistant internally glass-lined pipe. The internal surface of the pipe is initially treated to remove deposits which result from the pipe manufacturing process and from the atmospheric oxidation of the metal. This surface treatment is usually accomplished by sand or grit blasting the inner pipe surface utilizing conventional abrasive cleaning equipment.

Following the surface treatment of the pipe, a vitreous enamel forming frit powder dispersed in water is either wet sprayed onto the cleaned internal surface or is flow coated thereon by flushing an aqueous frit dispersion through the pipe. The glass ground coat thus applied is then dried. While less economical in manufacturing practice, a dry frit powder may be introduced into the pipe and by heating, rotation or other means may be caused to adhere to the internal pipe surface prior to firing.

When the wet applied powder has dried, the pipe is inserted into a furnace and the frit powder adhering to the inner pipe surface is fired during the initial stages of furnace firing to produce a vitreous enamel ground coat. The firing temperature of the ground coat is generally in the range of about 1500° to about 1650° F. With the assistance of refractory additions to the ground coat frit powder, the matured vitreous enamel surface thus produced is in a hard non-sticky condition, though the pipe is maintained at temperatures in the maturation range. The ground coat becomes chemically bonded to the pipe surface and acts as a sealer coat to which a glass cover coat may be readily chemically bonded.

The pipe is generally supported in the furnace on inclined rails or rollers so that it may be moved toward the cover coat station during the firing of the ground coat. Without removing the pipe from the furnace or appreciably reducing the temperature of the pipe, it is transferred to driving rollers at the cover coat application station. The rollers rotate the pipe while the cover coat glass composition is deposited on the interior surface of the pipe and usually during the maturation thereof.

The cover coat glass composition, which is a vitreous enamel forming frit powder, is deposited within the pipe by a tubular applicator. The applicator extends the full length of the pipe and is supported by the bottom of the pipe. Frit powder is deposited in the rotating pipe by an auger contained within the tubular applicator. The auger discharges the frit powder from the end of the applicator as it is gradually withdrawn from the rotating pipe. As the frit powder is tumbled uniformly over the entire inner surface of the pipe and reaches a temperature near that of the ground coat or below, it clings to the surface of the ground coat and becomes chemically fused thereto.

In some instances, due to the relatively great length and small diameter of a section of a pipe, it may be desirable to use a pair of frit depositing applicators, inserting one in one end of pipe and the other in the opposite end of the pipe. In other instances, it may be desirable to use a frit containing lance which would be rotated 180° to deposit frit powder along the full length of the pipe as the lance is rotated. Frit powder spray applicators may also be employed to uniformly apply a cover coat glass composition to the inner surface of the pipe. Due to the hard, non-sticky condition of the previously applied ground coat, the applicator employed may contact the ground coat surface along its entire length without marring or damaging the freshly ground coated surface.

On some occasions, it has been found to be desirable to employ cantilevered applicators which may be inserted into the pipe but out of extensive contact with the internal surface thereof. In pipe lengths of 20 to 30 feet or greater, and shorter lengths of relatively small diameter, such applicators inevitably develop a substantial degree of sag, even when cantilevered. Generally, the outer end of the applicator, due to this sagging tendency, invariably establishes frictional contact with the previously applied ground coat in varying degrees depending on pipe length and diameter. The relatively hard, non-sticky ground coat of the instant invention effectively resists the surface marring normally produced by such surface contact.

When the frit applicator has been withdrawn from the rotating pipe following completion of the cover coat application, the pipe is continuously rotated until the frit powder has been uniformly distributed over the entire

surface and until it has become fused to the ground coat surface and matured to provide a vitreous enamel corrosion resistant cover coat. The pipe is finally removed from the surface. Upon cooling, the glass lined pipe length is ready for immediate use or storage until such use is required.

FIGS. 2 and 3 illustrate a simple apparatus for applying a glass cover coat composition to the interior surface of a pipe 1. The pipe length 1 is positioned within a gas fired furnace 2, although other suitable heating methods, such as induction or resistance heating, may be employed. The pipe is supported on a series of parallel rollers 3 driven by shaft 4. Shaft 4 is connected to a drive means (not shown). By driving rollers 3 at a predetermined speed, pipe 1 can be rotated during the application of the cover coat glass composition and the maturation of the cover coat. Such rotation will insure uniform distribution of the cover coat material, resulting in a continuously smooth uninterrupted surface, and the rotation will maintain the heated pipe in a relatively straight condition during the firing phase.

The internal surface of pipe 1 is lined with the early maturing ground coat glass composition 5 of the invention. This coating is distributed over the entire inner surface of the pipe and is chemically bonded thereto. Coating or lining 5 serves as vehicle for chemically bonding a defect-free, corrosion-resistant vitreous enamel cover coat to the pipe.

A simple frit powder distributing tubular applicator 6 is shown within pipe 1. The applicator opens into the pipe at one end and into a hopper 7 at the opposite end. The hopper 7 contains a quantity of cover coat frit powder 8. An auger 9 extends from hopper 7 to the outermost end of applicator 6. The auger is driven by motor 10.

While the pipe is being rotated by rollers 3, the tubular applicator 6, with the assistance of insertion and withdrawal rollers 11, is inserted into the pipe and is permitted to rest on the rotating surface thereof. Auger 9 which is driven at a predetermined speed discharges frit powder 8 from the applicator onto the pipe surface as the applicator is gradually withdrawn from the pipe. The rotating action of the pipe acts to uniformly distribute the frit powder 8 deposited by applicator 6 over the entire internal ground coated surface 5. Upon maturation of the cover coat composition, a smooth uninterrupted corrosion-resistant vitreous enamel surface is produced.

While one type of applicator is shown, any apparatus which is designed to be inserted within a pipe to deposit a glass coating composition along the full length of a pipe, which has been previously ground coated with a hard, non-sticky ground coat composition, is considered to be within the scope of the invention.

One of the important advantages of the invention is shown in FIGS. 2 and 3. A simple, non-cantilevered covered coat applicator 6, which is fully supported by the ground coated pipe surface, may be used to apply the cover coat glass composition 8 to the pipe surface even though the applicator 6 is in substantial supporting contact with the freshly ground coated surface. The applicator 6 is, therefore, in substantial frictional contact with the ground coated surface 5 of pipe 1 during insertion of the applicator and during withdrawal as frit powder 8 is discharged from the applicator onto the rotating pipe surface.

The early maturing and hard, non-sticky ground coat of the invention is highly resistant to surface marring and damage resulting from such substantial contact of an applicator with a coated surface. This eliminates engineering problems in applicator design, enables the use of a greatly simplified applicator construction, avoids the necessity of designing elaborate aligning mechanisms and obviates the need for cantilevering the applicator. Each of the features permits the realization of substantial manufacturing economies.

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In developing the ground coat glass composition of the invention, it was determined that in addition to the components usually found in a ground coat composition, a mill addition of a refractory material would be required in the weight range of about 25 to 75%. The mill added refractory material could be one of the following materials or combinations thereof:

Oxides:	Vanadium
Aluminum	Tungsten
Silicon	Chromium
Calcium	Molybdenum
Magnesium	Nitrides:
Tin	Hafnium
Titanium	Tantalum
Zirconium	Boron
Hafnium	Zirconium
Cerium	Titanium
Beryllium	Uranium
Strontium	Thorium
Yttrium	Aluminum
Lanthanum	Barium
Cobalt	Beryllium
Manganese	Columbium
Molybdenum	Silicon
Nickel	Chromium
Niobium	Silicides:
Thorium	Tantalum
Vanadium	Columbium
Zinc	Tungsten
Chromium	Hafnium
Copper	Zirconium
Diatomaceous Earths	Vanadium
Gadolinium	Titanium
Holmium	Molybdenum
Samarium	Chromium
Barium	Oxide compounds:
Tungsten	Feldspar
Erbium	Bismuth Stannate
Europium	Alkali Aluminum
Gallium	Silicates
Germanium	Lithium Aluminum
Tantalum	Silicates
Thallium	Sodium Antimonate
Praseodymium	Aluminides:
Neodymium	Nickel
Borides:	Molybdenum
Hafnium	Chromium
Tantalum	Fluorides:
Zirconium	Fluorspar
Columbium	
Titanium	

The refractory materials enumerated are characterized by a melting temperature of 1600° F. or above. The refractory addition to the basic ground coat material, in addition to increasing the maturation temperature of the ground coat, affords the homogenous mass with a relatively high degree of initial stiffness. When the mass is wet applied to a pipe and dried, the resulting surface is relatively adherent. When the dried coating is heated to its maturing range, about 1550° to about 1650° F., the ground coat matures early in the heating cycle to produce a hard, non-sticky abrasion resistant surface at temperatures in the maturing range and below.

A typical basic ground coat composition of the instant invention will have components in about the following ranges:

Refractory materials	Percent
Alkaline earth metal oxides	35-55
Alkali metal oxides	1-10
Alkaline metal halides	10-25
Oxides of copper, chromium cobalt, manganese and nickel	1-7
Oxides of boron	0.5-5
	12-24

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A mill addition of a refractory material or combinations of refractory materials in the weight range of about 25 to about 75% is added to this basic ground coat composition to produce the ground coat composition of the invention.

A ground coat composition which has been found to produce successful results contains components in the following designated ranges:

		Percent
10	SiO ₂	38-42
	TiO ₂	0-3
	Al ₂ O ₃	2-5
	B ₂ O ₃	16-20
	CaO	2-6
15	Na ₂ O	15-19
	K ₂ O	0-4
	F ₂	2-5
	CuO	0-2
	NiO	0.5-1.5
20	MnO	0-1
	CoO	0.5-1.5

A refractory material or combinations of refractory materials in the weight range of about 25% to about 75% is mill added to the basic ground coat composition. The basic ground coat composition containing components with the above composition ranges can be expected to have a firing temperature in the range of about 1400° to about 1500° F.; and when the mill addition of refractory oxides has been added, the final composition can be expected to have a firing temperature in the range of about 1550° to about 1650° F.

In selecting a vitreous enamel cover coat, in addition to the general requirements that it provide a relatively smooth corrosive resistant surface which is chemically bonded to the ground coat surface, the cover coat should have a firing temperature about that of the ground coat firing temperature or below. Firing temperatures for the cover coat substantially in excess of the ground coat could be expected to deleteriously effect the properties of the ground coat and result in an undesirable pipe lining. A successfully employed vitreous enamel forming frit powder which will produce a continuously smooth uninterrupted corrosion resistant glass lining in combination with the above ground coat composition has components in the following ranges:

		Percent
	SiO ₂	62-67
	TiO ₂	1-5
50	ZrO ₂	5-9
	B ₂ O ₃	2-6
	Li ₂ O	1-5
	Na ₂ O	15-18
	K ₂ O	0-3
55	F ₂	2-5
	CoO	0.5-1.5
	NiO	0-1
	MnO	0-1

This composition can be expected to have a firing or maturing temperature which is below 1625° F.

In utilizing ground coat and cover coat compositions of the type described to line tubular articles, substantial economic benefits can be realized. A pipe coated according to the instant invention requires only one furnace phase and only a single cover coat application. After the wet ground coat has been applied and dried, the pipe is introduced into the furnace, and the ground coat is matured. While the pipe is still in the furnace, the cover coat is applied to the pipe, and this also is matured within the furnace. This not only appreciably reduces manufacturing time and expense but also reduces the amount of space required to glass line pipe thereby affording substantial operating economies.

Various modes of carrying out the invention are contemplated as being within the scope of the following claims

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particularly pointing out and distinctly claiming the subject matter which is regarded as the invention.

I claim:

1. In a method of applying a glass coating to the internal surface of a tubular member, the steps of mixing finely divided particles of a refractory material with a glass ground coat frit in an amount of 25 to 75% by weight of said frit to provide a ground coat composition, applying said ground coat composition to the internal surface of the tubular member, heating the member to a temperature sufficiently high to fire said frit and below the melting point of said refractory material, introducing an elongated applicator into said tubular member, supporting at least a portion of the applicator on the ground coat, discharging a glass cover coat frit from said applicator on the ground coat, and firing the cover coat frit to provide a smooth corrosion resistant coating on the internal surface of the tubular member.

2. The method of claim 1 in which the refractory material is selected from the group consisting of oxides, borides, fluorides, nitrides, silicides, aluminides and mixtures thereof, and has a melting point above 1600° F.

3. In a method of applying a glass coating to the internal surface of a tubular member, the steps of applying a first glass composition to the internal surface of the tubular member, said first glass composition comprising a glass frit and a mill added refractory material with said refractory material comprising from about 25 to about 75% by weight of said frit, heating the member to a temperature sufficiently high to fire said frit and below the melting point of said refractory material, introducing an elongated applicator into said tubular member, supporting at least a portion of the applicator on the first glass composition, depositing a second glass composition from said applicator on said first glass composition, and firing the second glass composition to provide a smooth corrosion resistant coating on the internal surface of the tubular member.

4. The method of claim 3, in which the glass frit contains from 35 to 55% by weight of refractory materials having a melting point above 1600° F.

5. The method of claim 3, in which the glass frit has a silica content in the range of 38 to 42% by weight of said frit.

6. In a method of applying a glass coating to the internal surface of a tubular member, the steps of applying a first glass composition to the internal surface of the tubular member, said first glass composition comprising a glass frit and a mill added refractory material with said refractory material comprising from about 25 to about 75% by weight of said frit and said refractory material having a

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melting point above 1600° F., heating the tubular member to a temperature in the range of 1500° to 1650° F. and below the melting point of the refractory material to fire said frit and provide a relatively firm and non-sticky glass coating at said temperature, introducing an elongated applicator into said tubular member while said tubular member is at said temperature and supporting at least a portion of said applicator on said glass coating, depositing a second glass composition from said applicator on said first glass composition, and firing the second glass composition to provide a smooth corrosion resistant coating on the internal surface of the tubular member.

7. The method of claim 6, in which the refractory material is composed primarily of silica.

8. A method of applying a glass coating to the internal surface of a tubular member, comprising the steps of rotating the tubular member about its axis, applying a first glass composition to the internal surface of the tubular member, said first glass composition comprising a glass frit and a mill added refractory material with said refractory material comprising from about 25 to about 75% by weight of said frit, heating the tubular member to a temperature in the range of 1500° to 1650° F. and below the melting point of the refractory material to fire said frit and provide a relatively firm and non-sticky glass coating at said temperature, introducing an elongated applicator into said tubular member while said tubular member is at said temperature and supporting at least a portion of said applicator on said glass coating, depositing a second glass composition from said applicator on said first glass composition, and firing the second glass composition at a temperature below said first named temperature to provide a smooth corrosion resistant coating on the internal surface of the tubular member.

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