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BRAZING PASTE

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8 Claims. (Cl. 148—22)

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This invention relates to improved furnace brazing pastes.

A wide variety of fabricated assemblies of various metals, alloys and metallic compounds melting appreciably above copper have been brazed heretofore by pre-positioning copper within or close to the joint to be brazed and then passing the assembly through a furnace in which it is heated to above the melting point of copper while being maintained in a reducing atmosphere. Under such conditions, the pre-positioned copper melts and is drawn by capillary action across the interface of the joint, thereby joining the parts of the assembly together through a copper bond. After the assembly has been cooled, preferably while maintained in a reducing atmosphere, a strong joint is obtained. This type of process has come to be known by the term "furnace-brazing." It has been found over the course of many years of experience that such furnace brazing operations produce best results when the joint clearance (i. e., the clearance between the parts of the assembly which are to be joined) is less than two or three thousandths of an inch. When such small joint clearances are provided, the molten copper is drawn into them very effectively by the wetting or capillary effect between the molten copper and the solid metal surfaces bounding the joint. This capillary action is of sufficient magnitude that the pre-positioned copper does not have to be in immediate contact with the whole of the joint which is to be brazed. All that is required is that the pre-positioned copper, when molten, contact at least a part of the joint. Capillary action then draws the molten copper into the whole of the joint (if enough copper has been supplied initially). The merits of furnace brazing processes are well understood in the art, and need little further explanation beyond pointing out that the metals, alloys, and metal compounds which have been so brazed include cast and wrought irons and steels, stainless steels, nickel, tungsten, and various metallic carbides.

In carrying out the furnace brazing processes in the past, the pre-positioned copper has been provided in the form of slugs, copper foil, pre-formed shapes of copper wire or strip, or sometimes in the form of a copper-powder paste in which copper powder is mixed with a vehicle such as water, alcohol, thinned nitrocellulose, or ordinary machine oil. Various disadvantages are found in the use of slugs, foils, or shaped wires or strips, since each requires that the particular shape needed for each joint of the entire assembly be cut, sheared, stamped, bent or otherwise

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formed to fit its particular joint. Such forming operations may involve considerable expense. Moreover, when such formed shapes are used, it is necessary for an operator to pick up one of such shapes and carefully position it in the assembly at the place where it is wanted. Frequently in picking up such a shape (e. g. a wire ring which is not fully closed), it becomes entangled with other pieces of the same shape, and time must be spent in untangling it from the others before it can be placed in the assembly. The time so lost may become a serious cost item where high rates of production are relied on to keep unit brazing costs low.

Brazing pastes have not been used as extensively in the past as have the pre-formed shapes, and generally have been used more on an experimental basis than otherwise, being used only where the more reliable foil or slug insert or pre-formed shape of wire or strip could not be applied. The pastes have not been regarded with favor because (*a*) they may dry out before or shortly after the assembly enters the furnace, to then allow the copper powder to fall out of the joint, (*b*) or because the vehicle softens under the heat of the furnace and the paste runs out of the joint, thereby producing an inferior joint while concomitantly depositing copper on areas where it is not wanted, (*c*) because the vehicle, when carbonaceous, leaves a carbon residue which may interfere with the formation of a strong joint, or which must be cleaned off of the brazed assembly before the assembly can be further finished (e. g. as by electroplating it with a desired finishing metal), or (*d*) because the pastes of the past have in most instances been difficult to keep in a uniformly-suspended condition, making it difficult to apply a predetermined quantity of copper to the joint.

I have now found that a brazing paste can be prepared by dispersing finely-divided copper oxide, metallic copper powder, or other joining metal powder in a synthetic hydrocarbon carrier of certain characteristics hereinafter described, which paste can be used in place of all of the previously used forms of copper, whether foil, slugs, pre-formed wire or strip shapes, or copper-powder pastes. My improved paste is substantially non-settling, is easily applied in predetermined quantities from suitable piston-type or pneumatic applicators, or by other devices, stays in place on the assembly while the latter is being heated in the brazing furnace, provides metallic copper which is drawn readily into the capillary joints, leaves little carbon residue, and forms a

clean, firmly-brazed joint. By using such paste, the expense and time-consuming operations involved in pre-positioning formed wire or strip shapes are avoided, and a brazing plant can stock just one supply of brazing copper for all types of assemblies, instead of stocking, as previously, a separate supply of copper for each particular assembly which is being brazed. Moreover when copper oxide is used to supply the brazing copper, the cost of such copper is considerably cheaper than is copper powder or than is the wrought copper in such forms as foil, wire and strip. In addition, I have found that the vehicle of my paste is harmless to the controlled atmospheres employed in furnace brazing, and permits assemblies to be brazed in any of the conventional furnace atmospheres without causing discoloration, carburization, decarburization or other chemical alterations of the surfaces.

Accordingly, it is an object of this invention to provide a brazing paste of the type described having the properties and characteristics described.

It is another object to provide an improved brazing paste composed essentially of copper oxide, copper or other joining metal suspended and dispersed in an organic vehicle, which paste leaves substantially no carbon deposit in the finished brazed joint.

It is a further object to provide an improved brazing paste of the type last described above which includes a substantially non-carbonizing film-forming material.

These and other objects will be understood from the following description of the invention.

I have found that a brazing paste having the advantages, characteristics and properties noted above can be prepared by dispersing copper oxide, metallic copper powder or powders of other joining metals or alloys in a gel-like organic polymeric vehicle which is characterized by being heat-depolymerizable so as to have low Conradson carbon values. Polymeric vehicles having this combination of characteristics produce a paste in which the copper or copper oxide is substantially non-settling, and which leaves substantially no carbon deposit on assemblies brazed or soldered in conventional furnace-brazing atmospheres. Petroleum vehicles have been used heretofore in brazing pastes, but to the best of my knowledge, the vehicles which have been used did not possess this combination of properties. Ordinary machine oil has been used, but the viscosity of such oil is not great enough to avoid settling, and it decomposes in the brazing furnace to deposit considerable amounts of carbon.

I have found that synthetic petroleum jellies are suitable for use as the vehicle in my pastes, and I prefer to use them because of their uniformity of composition and their low Conradson carbon residues. Such synthetic jellies generally have Conradson carbon values below about 0.5% and have viscosities on the order of 65 seconds (Saybolt-Universal) at 210° F. Other hydrocarbon jellies of comparable viscosity and carbon value are equally suitable but are not presently available commercially with the consistent uniformity of the synthetic products.

It will be understood that a low Conradson carbon value implies that the petroleum product, while cracking, forms volatile products at the temperautres employed in the Conradson test, instead of cracking to products which deposit carbon. The test is described in the A. S. T. M. Standards, 1946, part III–A, at page 120 under the A. S. T. M. designation D189–46. The synthetic hydrocarbon jellies are polymerized hydrocarbons, and the processes which are employed in their preparation separate from them such products as are prone to carbonize at the temperatures involved. Hence when such synthetic products are heated in a brazing furnace, they decompose again into their more volatile monomers, dimers, etc. without being cracked appreciably to such an extent as to deposit carbon. Many other organic vehicles having similar characteristics may be used as well. Broadly, the vehicles contemplated are the heat-depolymerizable organic polymers which are normally gels at room temperature and are capable of being depolymerized upon moderate heating, such as at temperatures below about 500° C. into monomeric or low molecular weight compounds which at such temperatures are vapors.

Various solvents, thinners or diluents may be used to vary the ultimate consistency of the finished paste, but the materials used for that purpose should preferably be volatile below about 500° C. without decomposing to produce any substantial amount of carbonaceous residue. For example, solvents such as ethylene glycol monoethyl ether acetate, diethylene glycol monoethyl ether acetate, benzene, certain higher alcohols, are useful. Various petroleum solvents or synthetic hydrocarbon polymer oils may be used to thin the synthetic hydrocarbon polymeric solids or gels. The solvents, thinners, or diluents may be employed in varying amounts as found to be necessary to form a composition ranging in consistency from a stiff paste to a paint-like liquid, due regard being given to the effect of the dispersed copper or copper oxide on the consistency of the final product.

It will be understood that when the brazing composition, after being applied to the assembly which is to be brazed, is heated in the reducing atmosphere of the brazing furnace, the solvents, thinners or diluents evaporate and the organic polymeric vehicle depolymerizes to low molecular or monomeric state in which it vaporizes readily. Therefore, substantially no part of the organic vehicle decomposes to leave a residue of carbon in the joint or its immediate vicinity. Such decomposition necessarily occurs before the melting point of the copper powder is reached so that the atmosphere of the brazing furnace has free access to all parts of the intended joint and can accomplish its function of reducing any metallic oxide films thereon and providing clean metallic surfaces which the ultimately molten copper can wet and braze.

The relative proportions between copper oxide, copper or other joining metal powder and polymeric vehicle may be varied rather widely although it is preferable to include as much copper or copper oxide in a given quantity of vehicle as will yet yield a pasty, non-settling product which can be readily applied. For example, I have mixed 20 lbs. of fine cuprous oxide with 4 lbs. of a polymeric hydrocarbon gel and have obtained a smooth paste without using any thinners or diluent. The paste can be extruded readily from the $\frac{1}{8}$ inch diameter orifice of a piston-type textile oiler of the type now widely used for lubricating textile machinery. Stiffer pastes or thinner ones can be prepared as well, and the proportions may be varied to suit one's needs. Generally the aim is to have the joining metal content as high as possible so that the amount of vehicle employed will be a minimum, since the

vehicle serves no purpose in the brazing furnace other than that of keeping the joining metal in its intended position in the vicinity of the joint. It is not intended to function as a reducing agent for any copper or other oxide which may be in the paste since such reduction may lead to decomposition and carbonization of the volatile monomers or of the other low molecular weight products resulting from heat-depolymerization of the organic vehicle. Some reduction may occur; however, most of the reduction of the copper oxide tends to occur at temperatures above the effective heat-depolymerization temperature of the polymeric vehicle, being effected either by iron or other metals of the assemblies being brazed, or by the reducing atmosphere of the furnace, or both.

Under some circumstances encountered in brazing plant operations, an assembly may be prepared for brazing a day or more ahead of the time at which it enters the brazing furnace. During this time interval, non-drying brazing pastes may be accidentally displaced from their intended positions on the assembly. To overcome this it is desirable under such circumstances to add a film-forming material to the paste so as to make a paste which in the course of a few hours or so of exposure will dry or set to at least a soft, tenacious film. In recent years synthetic unsaturated drying hydrocarbon polymer oils of low Conradson carbon values have become available, and I particularly prefer to use such polymer oils as the film-forming ingredient.

The following example illustrates the principles of my invention.

Example

One gallon of paste was made by thoroughly mixing 20 lbs. of bright red cuprous oxide into 4 lbs. of a synthetic polymeric heat-depolymerizable hydrocarbon jelly. The mixture was stirred for about one hour to produce a smooth paste. The polymeric hydrocarbon vehicle was prepared from an unctuous jelly-like synthetic hydrocarbon material having the characteristics of a petrolatum. Its properties were as follows:

A. P. I. gravity_____degrees appr__	33.0
Flash, ° F. minimum_____appr__	350.0
Fire, ° F. minimum_____do____	400.0
Viscosity S. U. at 210° F_____do____	65
Melting point, ° F_____	115/125
Conradson carbon___per cent appr__	.19

The petrolatum was thinned by blending with about 8 parts thereof about 2 parts of a synthetic polymeric heat-depolymerizable hydrocarbon oil having the following properties:

A. P. I. gravity_____degrees__	25–30
Flash, ° F_____	270–300
Fire, ° F_____	310–340
Viscosity at 100° F. (S. U.)____seconds__	55–65
Conradson carbon_____per cent__	.01

The finished vehicle had the following properties:

A. P. I. gravity_____degrees__	32.0
Pour point_____do____	115
Flash, ° F_____	330
Fire, ° F_____	375
Viscosity at 210° F. (S. U.)_____seconds__	51.0
Conradson carbon_____per cent__	.16

This vehicle, and others having Conradson carbon values below about .5% and preferably below about .25%, may be used with a variety of other joining-metal powders such as brass powder, powders of low melting silver solders, powders of binary phosphorus-copper brazing alloys, powders of ternary or more complex phosphorus-copper brazing alloys, powders of silver-rich silver alloys, powders of nickel-silver alloys and other spelter solders, powders of cadmium-nickel solders, powders of soft solders, etc. Any metallic solders or brazing metal which can be produced in the form of a powder can be used to make soldering or brazing pastes in accordance with my invention.

Having described the invention, what is claimed is:

1. A substantially non-setting furnace brazing paste comprising essentially a minor amount of a polymeric heat-depolymerizable hydrocarbon gel vehicle characterized by having a Conradson carbon value below about .5%, and a major amount of finely-divided copper oxide dispersed in said vehicle.

2. A paste as claimed in claim 1 wherein the Conradson carbon value is below about .25%, and wherein the organic gel vehicle is composed of synthetic polymeric heat-depolymerizable hydrocarbon materials.

3. A substantially non-setting joining-metal paste comprising essentially: a minor amount of a synthetic polymeric heat-depolymerizable hydrocarbon gel vehicle having a Conradson carbon value below about .5%; and a major amount of joining-metal powder dispersed in said vehicle.

4. A paste as claimed in claim 3 wherein the Conradson carbon value of said vehicle is below about .25%.

5. A paste as claimed in claim 4 wherein the joining-metal powder is a copper-base powder.

6. A paste as claimed in claim 4 wherein said vehicle includes sufficient synthetic unsaturated heat-depolymerizable hydrocarbon drying oil to cause said paste to dry on exposure to air to at least a soft coherent film.

7. A furnace brazing paste composed essentially of: about 4 parts by weight of a gel vehicle composed of synthetic polymeric heat-depolymerizable hydrocarbon materials; and about 20 parts by weight of finely-divided red cuprous oxide dispersed uniformly in said vehicle.

8. A paste as claimed in claim 7 which includes sufficient synthetic polymeric heat-depolymerizable unsaturated hydrocarbon drying oil in said vehicle to cause said paste to dry on exposure to air to at least a soft coherent film.

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