

[54] **INTEGRAL HEATING ELEMENTS**

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[56] **References Cited**

UNITED STATES PATENTS

2,942,992 6/1960 Dumesnil 106/48

3,149,002 9/1964 Place et al. 252/514 X
3,396,055 8/1968 Hedden et al. 252/514 X
3,440,182 4/1969 Hoffman 106/48 X

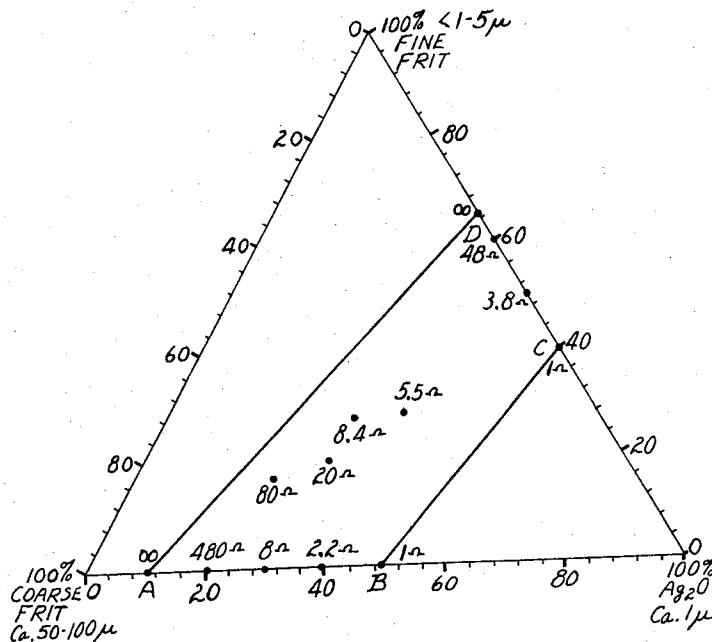
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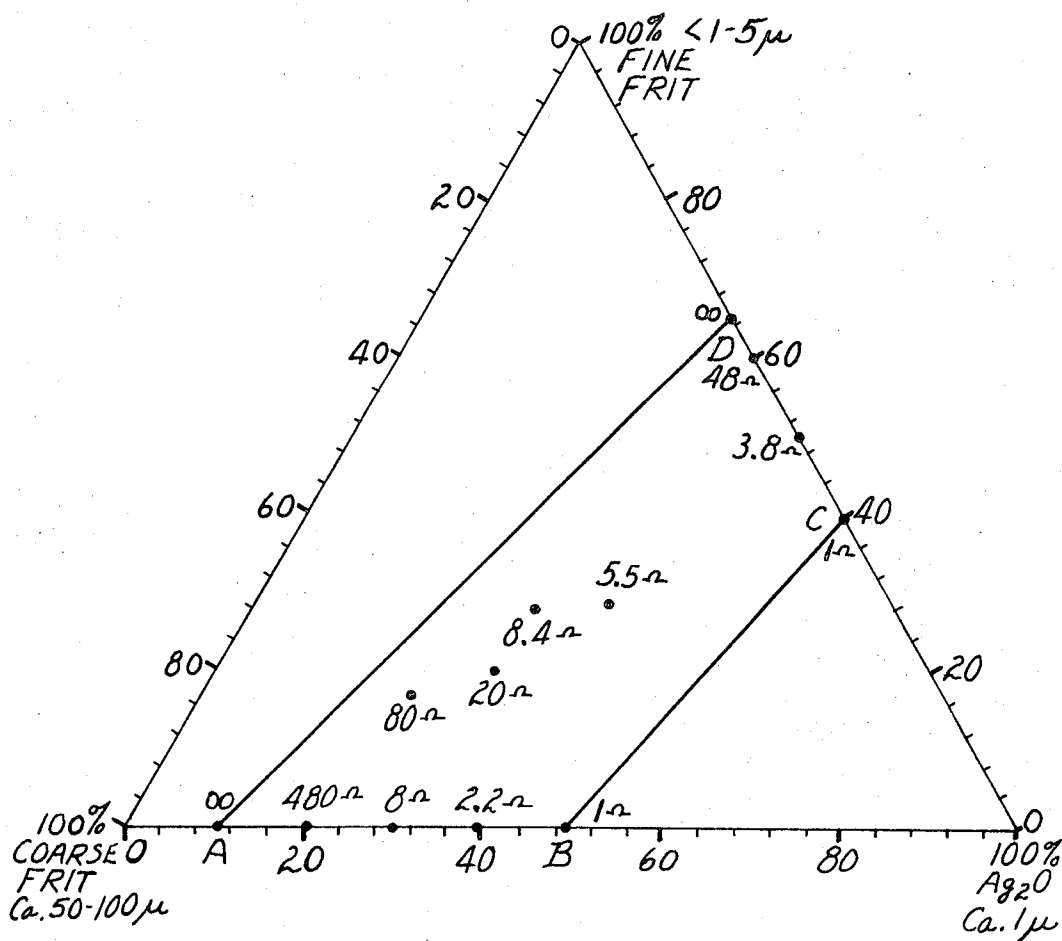
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ABSTRACT

Combinations are provided of organic binder, metallic particles, or powder converting to a metal under mild reducing conditions, and porcelain enamel frit, preferably in a range of sizes, at least a part of which has average particle diameters which are at least 5 times the diameters of ultimate metal particles. These combinations are used to apply integral heating elements to various utensils.

10 Claims, 1 Drawing Figure





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INTEGRAL HEATING ELEMENTS

This invention relates to new combinations useful in producing resistance element or integral heating elements and to processes ancillary to the use of such combinations in producing electrically heated dishes, vessels, utensils, etc. In particular this invention relates to the novel combination of porcelain enamel frits and silver oxide or noble metal particles with a fugitive noncarbonizing organic binder in which at least part of the porcelain enamel frit is larger by at least 5 times, e.g., 5 to 10 times than the conductive particles.

Here and elsewhere silver oxide is considered in particular. It must be recognized that, on firing, silver oxide is converted to silver metal in finely divided form. It will be understood that other conductive metals are generally similar when of comparable particle size except as for the necessity for reduction. Silver oxide provides very fine particles of silver of the order of less than 1 micron in diameter.

It is well known in the art to combine metal powders and glass frit. Such compositions are commercially available in proportions adapted to give conductive films or thick film conductors, resistances, etc. Such compositions are generally of value over very narrow changes in composition i.e., a very small percentage change effectively renders a composition either excessively conductive or substantially very highly electrically nonconductive. These compositions moreover provide narrow electrical paths like wires so that use thereof for heating shells limits the area of the sheet to which heat can be supplied.

It has been found that compositions prepared to contain silver oxide particles and porcelain enamel frit particles in a range of larger sizes are adaptable to relatively wide variation in composition while providing resistance films which may be fired as an integral part of a vessel or utensil, for example, for serving food. These compositions and their uses thus fulfill objects of the invention.

It is found that the frit particles should be of a size range of which a substantial part is five or more times the average size of the metal (i.e., Ag₂O) particles. It is possible for a small portion of the frit particles to be of the same magnitude as the smallest metal particles or even smaller. In the following discussion some speculation is made as to the reason that such novel compositions are so effective but the reasons are not entirely clear. Thus, it is found that, after firing, the porcelain enamel matrix can be dissolved away from the embedded silver and a frangible reticulum is obtained. The reticulum appears to be composed of innumerable minute particles of silver which contact one another but are not generally fused into relatively massive wires or sintered together.

Because of the multiplicity of contacts in the network the heating elements obtained are thus less subject to mechanical or electrical breakdown because breaking of even several contacts does not throw so much load on parallel contacts as to cause melting and breakdown with failure of the heating element. Instead the load is slightly increased over each contact. It is only when a substantial number of the contacts are severed that the electrical load causes breakdown. Such a situation may occur where contact is made to a heating element. At the junction there may be relatively high current density and a tendency to burn out connections. This is overcome by providing graded contacts in which a metal-rich composition is applied at points of contact. This provides innumerable contacts through a network and distributes the electrical load to the heating element.

Reverting to the compositions employed in these novel heating elements, the compositions are illustrated by a drawing, which is a three-component diagram in percents by weight of various compositions fabricated into heating elements of the same dimension by the procedures hereinafter described.

Separate coarse and fine frit components are used for convenience in illustrating more clearly the effects of variations in the proportions of frit particles which are much coarser than the silver oxide particles. It will be seen that generally even broader ranges of compositions are effective using the rela-

tively coarse frit than using the finer frit. The finer frit is, nonetheless, coarse in comparison to the silver oxide. The usual combinations of the prior art are so prepared that the metallic component is very likely to be in the size range of the coarsest particles.

The preferred compositions of the invention are those lying in the general area ABCD away from extreme edges AB and CD, that is those which are neither all coarse or all fine but are average and more similar to a simple milled frit. In this figure the line AD represents compositions having essentially infinite resistance and line BC represents compositions having approximately 1 ohm resistance in the size of conductor illustrated. If sufficient points were determined it is quite possible that these lines might bow or bulge to some extent. It will be obvious that such a graph is highly specific and that other graphs can be constructed experimentally based on the present teachings from many specific combinations of frits and conductors and that empirical differences will probably be found. The purpose is to illustrate especially the use of coarser frit particles than metal particles. It is believed that no one has heretofore discovered that such a broad range of compositions can be used which furthermore permit great flexibility in electrical design with relatively easy retention of the intended characteristic parameters of dimensions and watt rating. Thus it will be evident from the graph that broader ranges of composition are useful than has been general heretofore using low-temperature glassy frits milled to being generally as fine as or finer than the metal particles. This appears to be an advantage of using coarser frits and recrystallizing porcelain enamels.

In the drawing, the apices are designated as 100 percent of the respective components the increasing percentages of which are indexed along the adjacent sides. Each apex is, of course, also 0 percent of both other components. The various points represent compositions which are marked with the resistance in ohms of an element about 125 cm. long, about 6 mm. wide and about 0.125 mm. thick produced as described hereinafter. These resistances are termed specific element resistances for convenience. It will be seen that the specific element resistances increase rapidly at lower contents of silver and decrease above 50-60 percent silver to the point of being excessively conductive. It will be evident that any desired combination of properties can be attained within these teachings using greater or lesser amounts of porcelain enamel frits depending on the resistance, thickness, width and length of conductor desired.

The silver oxide used for these compositions, and generally useful and preferred in such compositions averages around 1 micron in particle size with smaller particles as low as 0.5 micron and occasional particles up to about 2 microns. Such material is readily available in chemically pure grades.

The preferred matrix material is a porcelain enamel which is compatible with the base to which the heating element is to be attached. A commonly available and generally useful enamel is a moderate phosphate content enamel containing about 15-20 percent of titania. A typical such composition is:

	% by weight
Dehydrated borax	19.1
Quartz	42.0
Sodium nitrate	7.8
Sodium silicofluoride	1.2
Potassium silicofluoride	7.8
Anhydrous sodium monophosphate	3.2
Titania	18.9

So far as is known the composition as such is not critical although it is characteristic that the compositions recrystallize and mature at a low enough temperature so that the metal does not coalesce and flow together. Thus, the enamel is non-fluxing for the metal. It is at least possible that recrystallization of the titania opacifier may decrease flow. In any event, it is preferred that a porcelain enamel frit be used in compositions for producing heater elements on metal utensils.

As obtained, frits are usually obtained as glassy flakes or granules which must be milled and then give distribution of particle sizes. In order for compositions of the invention to be effective the particles of the milled frit must be predominantly usually 80–85 percent or more, larger by a factor of 5 or more than the average size of the metal particles. The frit may be milled by any convenient method. It may be convenient to screen the coarsest particles from the frit and then further mill them to smaller particles. In the compositions used in construction the drawing, the coarse particles passed 150 mesh and were held on 270 mesh, that is they were between 53 and 105 microns in diameter. The frit used for the fine component was extensively milled (in ethanol for 5 hours or longer) to be of a size range from less than 1 micron to 5 microns with some particles up to 10 microns.

A particularly useful embodiment of the invention is in transfer sheets of frit which can be applied to a vessel and fired in place. This offers some valuable conveniences in fabrication. In this embodiment, frit of suitable particle size and silver oxide are combined with an organic binder which decomposes on heating without charring or coking and a solvent for the binder. A small amount of plasticizer may be included if desired. The thick composition is cast or knife-coated to a desired thickness e.g., 0.05 to 3 mm. on a smooth support such as glass, polished metal, silicone or polyethylene impregnated paper or a polymeric film. The solvent is then evaporated. Naturally, because of the valuable metal contents of these compositions thinner films are preferred but it should be noted that a much lower metal content may be useful in a relatively thicker film. Thinner films down to about 0.01 mm. are conveniently prepared directly on a utensil or for transfer from backings using silk-screening processes.

In this embodiment it appears that the range of particle sizes of frit helps to entrap the silver particles so that they do not segregate or settle under the influence of gravity during drying. The binder also retards segregation of silver particles so that a homogeneous suspension is retained. For example, the compositions used in constructing the drawing were prepared from 100 grams of the dry combination in the various proportions as shown in the figure of frits and silver oxide suspended in a solution of 20 grams of polyisobutylene (available as Vistanex L-120 having average molecular weight 120,000) in 50 grams of toluene. Other binders may also be used as alternatives or other solvents. The composition is knife-coated to about 0.6 mm. on a silicone-treated paper support sheet and air-dried. Dairing may be applied to the suspension before the coating operation but is not necessary in most instances. Entrapment of air bubbles in porcelain enamels is frequently considered to provide a measure of stress relief.

After drying the film or tape of the composition may be rolled upon itself into rolls for storage and later use or it may be used directly.

It is convenient to cut the tape to sheets, for example 7.5×12.5 cm., which fit a particular utensil or are adapted to provide a heating element of particular output. Naturally if the backing on which the film is cast is glass or metal, the film must be peeled away first. Alternatively, when cast on treated paper or polymer-film as above, the backing may be retained to give additional support and removed after transfer of the film to the utensil to which it is to be adhered.

The film, for example in the cut sheet, is converted to a serpentine or meandered heating element by making suitable cuts to subdivide the surface into the desired pattern which may be arranged to have terminals at opposite ends or the same end or in other desired configuration by scoring the film in any convenient manner with a knife or by stamping, dinking or other such procedure. It is not imperative that the cuts pass entirely through the film as natural shrinkage on firing will tend to open the cut and, furthermore, the first passage of current will burn out weak connections leaving the reticulation or filigree of metallic conductor intact in those parts of the film which were uncut. Consequently cuts may be made in the film while retaining a backing sheet to provide support. Cuts can

also be so made as to provide a shape which will be readily fitted to a vessel having a nonplanar surface by cutting away certain parts and scoring other parts. This procedure enables application of integral heating elements, for example, to 10×15 cm. rectangular dishes 2.5 cm. deep used in serving food in air flights. It is also possible to defer making cuts until the entire sheet has been affixed to a base.

Adhesion of the film to a base is conveniently effected using a small amount of the organic binder in the same solvent as an adhesive. Thus in preparing heating elements for constructing the drawing, approximately 7.5×12.5 cm. pieces of film on silicone-impregnated paper are applied to 10×15 cm. pieces of porcelain-enamelled steel using a solution of polyisobutylene in toluene (about 10 percent by weight) as adhesive followed by scoring with lines at 6 mm. intervals starting 6 mm. inside the left or right margin alternately and running to the opposite 12.5 cm. side to give a serpentine or meandered pattern with 20 legs each 6.3 cm. long so that the total pattern is about 125 cm. It will be recognized that 6 mm. at each side is not calculated in the leg. Elements of this size are suitable for application to the above-described rectangular dishes.

It will be recognized that electrical insulation must be maintained between the heating element and the steel or metal of the vessel. A flat steel sheet as described above would be a utensil for certain purposes, as for example, warming a biscuit. The insulation as provided above is the porcelain enamel which desirably is the same as that employed in compounding the heating elements film. The final utensil thus has a metallic shell, a porcelain enamel insulating layer and an integrally bonded heating element. Other insulative materials may be employed and, because the temperatures to be employed are generally not very high (frequently below 100° C. during operation is heating elements and rarely up to 200° C. except when especially electrically resistant undercoatings are used), it is not necessary to limit compositions to the extent required for high-temperature insulative glazes and ceramics.

Firing of the assembled utensil and film proceeds in two stages. During the first stage the binder is depolymerized leaving the unsintered frit and silver or silver oxide as a residue. This is accomplished readily by firing the above specimens up to about 600° C. during 15 minutes. This is followed immediately by firing to the maturing temperature of the particular porcelain enamel employed, e.g., 800° C. for 3 minutes. Prolonged heating at higher temperatures may result in greater flow of the enamel and is therefore generally avoided. Firing is for a sufficient time to effect maturation of the enamel including recrystallization which may occur normally or even to some extent at a lower temperature stage.

During that stage of firing when there is no binder present, a heating element which is not lying flat may tend to drop away or spall. It is found that such undesirable effects are conveniently counteracted by employing a small amount (1–10 percent) of a low-temperature glass, such as a lead borosilicate glass, as fine particles in the polymer-solvent adhesive combination. This low-temperature glass is preferably one which melts below the temperature at which the polymer is entirely decomposed, for example, 300° to 500° C. The small amount involved is sufficient to adhere the heating element film without fluxing the silver so that the latter will flow. The silver is thus embedded in a substantially nonfluxing matrix.

As noted above, it is convenient to provide contacts to the heating elements of the invention by application to the terminals of a more metal-rich composition. This is done before firing so that all firing operations are conducted at once. A small piece of film or wire or a small amount of a paste of the desired metal-rich composition is applied wherever terminals or taps are desired. Moistening with solvent and slight pressure is sufficient to assure contact. Leads can be connected to the heating elements in whatever manner or by whatever means is then compatible with the equipment being employed. For example, when using a heating element which is 65 percent porcelain frits and 35 percent silver oxide, contact spots are applied using a film which contains equal weights of frits

and silver oxide. After firing the film which was originally 0.6 mm. thick has shrunk to about 0.10 to 0.15 mm. thick and is thicker where the metal-rich spot is provided. For measuring resistances, contact is made using metal strips held in place by spring clips or wire leads are soldered to the metal-rich tab or spot.

What is claimed is:

1. A film adapted for application of a conductive pattern to a utensil consisting essentially of depolymerizable organic binder, very finely divided metallic or metal-yielding conductive powder and recrystallizing porcelain enamel frit having particle sizes substantially five or more times as large as those of said conductive powder in a range of sizes between about 1 micron and about 100 microns.

2. A film according to claim 1 wherein the recrystallizing porcelain enamel frit has particle sizes predominately falling within the ranges in which the average diameter is from 5 to 10 times the average diameter of the particles of conductive powder.

3. A film according to claim 2 in which the metal-yielding conductive powder is silver oxide with particle size of about 0.5 to 2 microns, the organic binder is polyisobutylene and the porcelain enamel frit is composed of recrystallizing frit containing titania and is predominately in two sizes of 1-5 microns and 50-105 microns.

4. A composition adapted to firing to conductive patterns comprising recrystallizing porcelain enamel frit having parti-

cles in a range of diameters predominately falling within the range of from about 5-10 up to 50-100 microns and silver oxide having an average diameter of about 0.5 to 2 microns.

5. A process for production of electrically heated utensil comprising the step of adhering to a utensil coated with porcelain enamel a coating comprising recrystallizing porcelain enamel frit in proportions of from about 85 to about 50 percent of frit and silver oxide in proportions of about 15 to about 50 percent.

6. A process according to claim 5 wherein the coating is applied in the form of a film containing depolymerizable organic binder.

7. A process according to claim 6 wherein adhesion of the film is enhanced by application of an adhesive of depolymerizable organic binder in solvent therefor containing 1-10 percent by weight of low-melting lead borosilicate glass.

8. A process according to claim 7 wherein connection spots are provided by application of metal-rich film over portions of the film where contacts are desired.

9. As an article of manufacture the combination of a porcelain enameled utensil and an electrically conductive heating element, the fired product of claim 1, bonded to said utensil as an overlay embedded in the porcelain enamel thereof.

10. A film according to claim 1 in combination with a supporting backing.

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