Nov. 25, 1969 C. H. LYNGE 3,480,461

METAL ARTICLES HAVING POLYTETRAFLUOROETHYLENE COATED PRESSING SURFACES AND METHODS OF THEIR MANUFACTURE

Filed Nov. 14, 1966 2 Sheets-Sheet 1

Fig. 1.

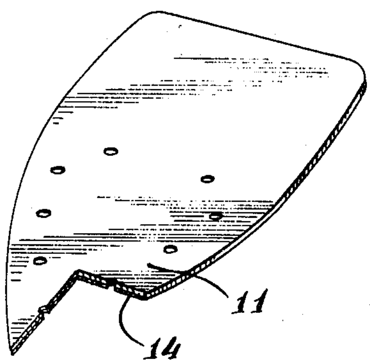

Fig. 2.

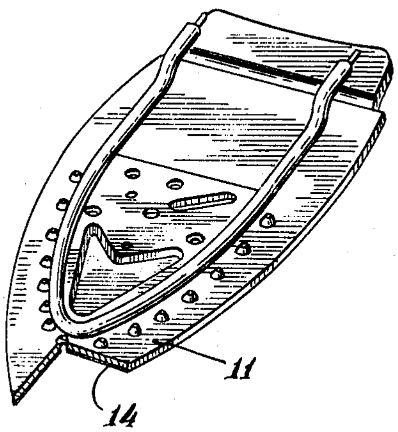

Fig. 3.

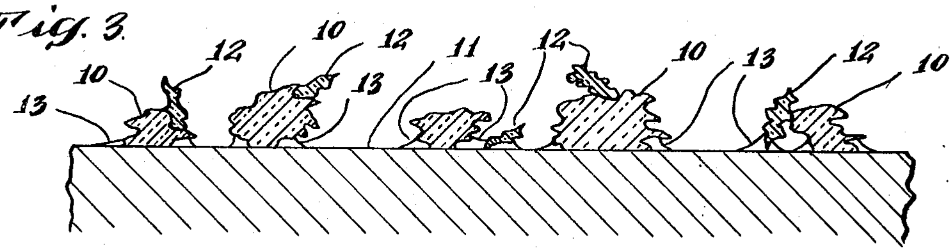

Fig. 4.

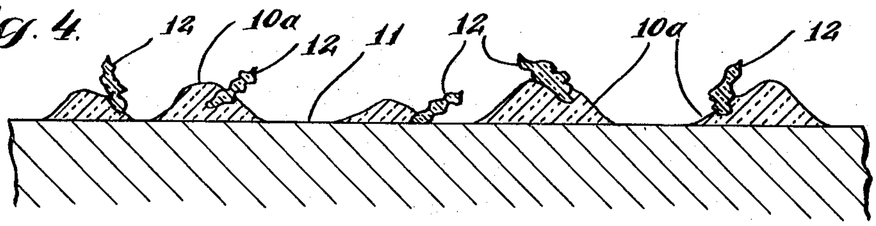

Fig. 5.

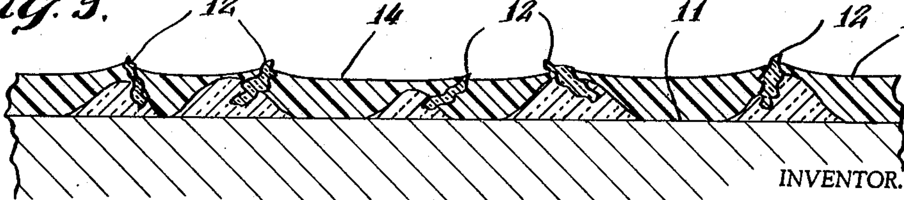

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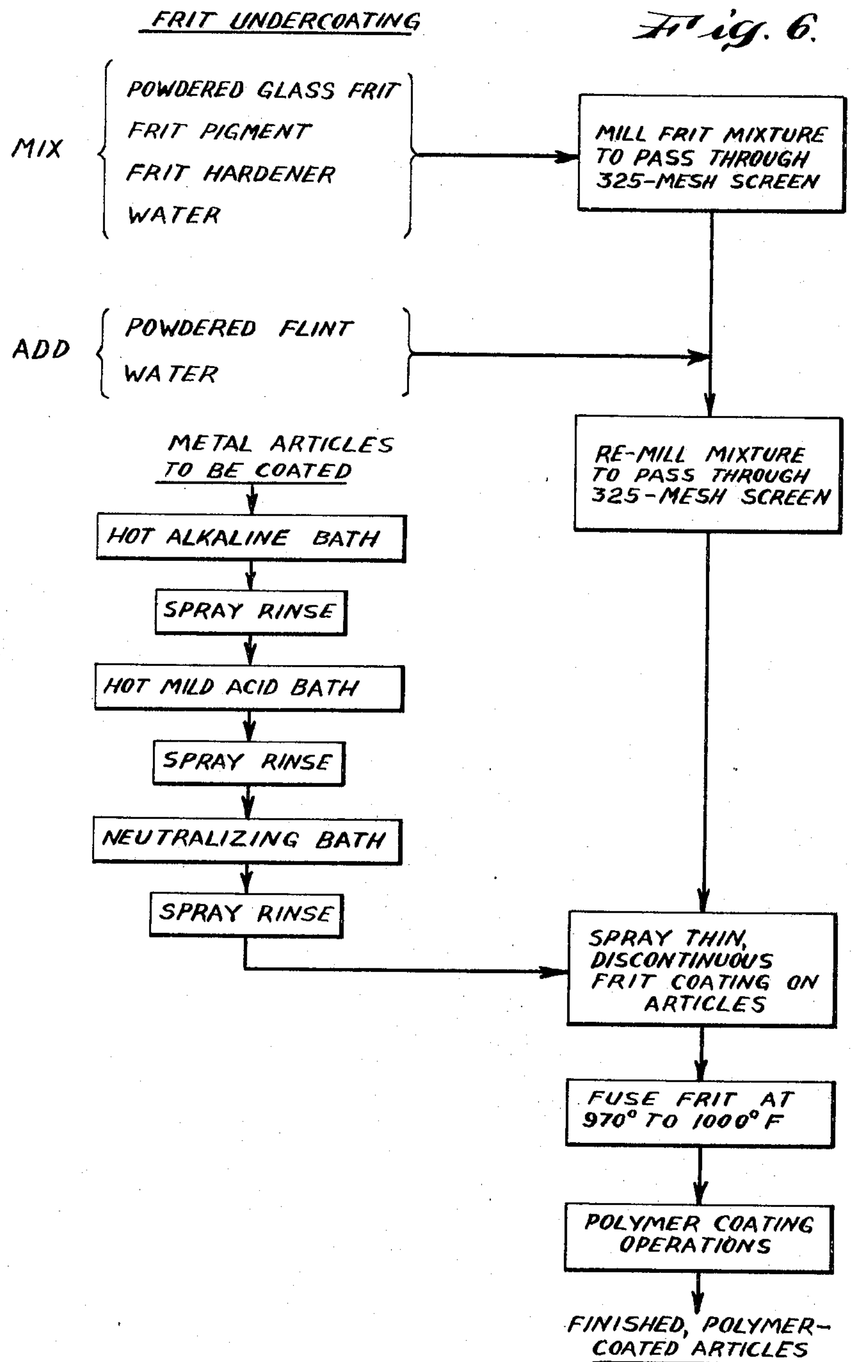
Fig. 6.



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METAL ARTICLES HAVING POLYTETRAFLUOROETHYLENE-COATED PRESSING SURFACES AND METHODS OF THEIR MANUFACTURE

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ABSTRACT OF THE DISCLOSURE

"Teflon" coated metal objects and methods and compositions employed in their manufacture. Clean, smooth metal surfaces are provided with an intermittent, discontinuous coating of a multiplicity of separate, discrete, independent bodies of ceramic material incorporating a minor proportion of unfused flint glass particles, and a thin coating of polytetrafluoroethylene surrounds the major proportion of the overall height of the fused ceramic bodies. Protruding unfused flint glass particles serve to anchor the polymer coating, prevent snagging or peeling, and provide wear-points or "bumpers" for contacting abrading objects, producing polymer-coated articles having significantly extended useful lives.

This invention relates to metal articles having surfaces coated with smooth polymer materials such as polytetrafluoroethylene, marketed by Du Pont as "Teflon," and particularly to articles such as cooking utensils and permanent and auxiliary soleplates for commercial pressing devices and domestic steam and dry irons which are provided with a smooth, low-friction "Teflon" coating securely bonded to their pressing surfaces to provide unusually long-wearing characteristics.

The increasing popularity of grills, pans and other cooking utensils with "Teflon" coatings has produced an increasing demand for both cooking utensils and pressing devices such as domestic steam and dry irons having these smooth, low-friction coatings on their active surfaces. Conventional polymer coatings of "Teflon" and like materials applied to the smooth metal surfaces of such utensils are easily chipped and peeled away from such surfaces during use and they are easily abraded by scouring and by stirring with metal spoons or the like. Accordingly, such "Teflon"-coated utensils require extreme care during use to avoid wear and damage to the coated sudfaces.

A further problem encountered with the conventional die-cast aluminum soleplates of domestic steam and dry irons apparently results from the internal structure of the metal underlying the smooth, die-cast surface, where entrained gases and included voids and cavities are apparently produced by the quick chilling of the molten aluminum contacting the smooth surface of the die during the casting process. Such internal voids and cavities underlying the smooth, die-cast surface may exhibit no visible indication thereon. However the heating of these die-cast aluminum soleplates required during the "Teflon" coating process to fuse and bond the polymer coating thereon produces blisters, buckling, cracks and roughness on the die-cast surface destroying its usefulness, apparently caused by the expansion of the included gases during this subsequent heating of the die-cast articles.

The use of polymer "shoes" and removable "Teflon"-coated metal shoes for such pressing devices as steam and dry irons has been proposed in various issued patents, but satisfactory techniques for bonding such polymer coatings to smooth metal surfaces, particularly to smooth

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aluminum pressing surfaces, has never been achieved before the present invention.

It has now been discovered that such polymer coatings may be firmly and securely bonded to smooth metal surfaces with the compositions and coating techniques of the present invention. These techniques do not require extensive roughening, sandblasting or deep etching of "gripping" cavities in the surfaces to be coated, which can thus be extremely smooth, and which also have the added advantages of a smooth, long-wearing low-friction "Teflon" coating. The pressing devices of this invention afford easy, low-friction pressing or ironing, generally avoiding the "shine" often produced by the pressing operation on slightly worn fabrics.

In the coating techniques of the present invention, the smooth, metal surface to be coated is first cleaned, using suitable mild acid or alkaline cleaning solutions to eliminate all accumulations of oxides, oil, grease or other foreign substances and to leave the clean, bare metal surface exposed.

Next, a partial, discontinuous coating of finely powdered glass-like "frit" is applied and fused to the bare metal surface. Highly superior bonding or "gripping" of the final polymer coating applied over this discontinuous fused frit is produced when the frit contains a small proportion of between about 2 and about 10 percent, and preferably about 4 percent, of finely milled particles of "flint glass," extremely hard glass having a high melting point, whose particles are characterized by angular sharp-edge fracture surfaces, and dendrite-like corners or extremities which can be fused and rounded only by very high temperatures.

Inclusion of "flint" among the finely milled glass particles to be applied to the bare metal surface to create a fragmentary, discontinuous, ceramic "porcelain"-type coating provides excellent bonding adherence for the overlying polymer coating thereafter applied.

While it is difficult to verify the reasons for the unexpected success of the coatings applied by the techniques of this invention, it is believed that the particles of flint included in the discontinuous porcelain frit remain substantially unfused, with their sharp corners, points and edges extending above the rounded fused porcelain patches produced by the high temperature fusing of the other frit particles. It is further believed that these sharp, angular flint protrusions achieve two desirable effects: They apparently provide barbs or anchors gripping the overlying polymer coating thereafter applied at a multitude of points, anchoring it firmly and securely to the supporting metal surface and strongly resisting any scratching, chipping or peeling of the polymer coating from the metal surface by contact with other objects. In addition, some of the sharp, angular flint particles apparently extend beyond the outer surface of the polymer coating to provide "bumpers" or extremely hard wear points on which the coated surface rides during use, thus further avoiding chipping, peeling, snagging or gouging of the "Teflon" coating by external surfaces with which it may come in contact.

Accordingly a principal object of the present invention is to produce metal objects provided with firmly bonded, long-wearing polymer coatings.

Another object is to provide economical and easily reproduceable coating methods for applying low-friction, polymer coatings of polytetrafluoroethylene and like materials to smooth metal surfaces.

A further object is to provide permanent and auxiliary soleplates for domestic steam and dry irons having firmly bonded, long wearing coatings of "Teflon" which are highly resistant to chipping, peeling, scratching or wearing away by continued use.

Other and more specific objects will be apparent from the features, elements, combinations and operating procedures disclosed in the following detailed description and shown in the drawings, in which:

FIGURE 1 is a perspective view of a thin, auxiliary metal soleplate provided with a smooth polymer coating applied by the techniques of this invention and designed to be mounted on the underside of a conventional steam iron;

FIGURE 2 is a perspective view of a heavy metal soleplate similarly provided with a "Teflon" coating on its lower pressing surface by the techniques of this invention, and designed to be incorporated in a domestic steam iron;

FIGURES 3, 4 and 5 are greatly enlarged, cross-sectional elevation views showing the metal surface and the discontinuous frit coating thereon during successive stages of the polymer coating processes of this invention; and,

FIGURE 6 is a schematic flow diagram illustrating the successive operations required in the processes of this invention.

The auxiliary soleplate shown in FIGURE 1 and the permanent soleplate shown in FIGURE 2 are both designed to serve as the supporting bases and pressing surfaces for domestic steam irons, and their undersurfaces are provided with smooth, low-friction, long-wearing coatings of polytetrafluoroethylene or like polymer materials by the techniques of this invention. It is important to avoid the ruptured, buckling surface roughness produced on smooth die-cast aluminum surfaces by the temperatures required to fuse "Teflon" coating thereon, and particularly by the higher temperatures required for using porcelain-type frit undercoatings thereon. Therefore the permanent and auxiliary soleplates of the present invention are formed of rolled aluminum plate or sheet material having equally smooth surfaces combined with uniform, homogeneous grain structure throughout the body of the material, avoiding or minimizing included voids or gas bubbles which may result from the quick chilling of the melt as it contacts the cold smooth molding die-surfaces in a die-casting machine.

These rolled aluminum plates or sheets are provided with lower pressing surfaces of the desired degree of smoothness, either by final passes through polished rolls in the rolling process, or by subsequent polishing with very fine abrasives. They are then subjected to successive operations of surface cleaning, "frit" coating, and final polymer coating procedures in the manner now to be described in detail.

SURFACE CLEANING PROCEDURES

When the metal parts to be coated are substantially free of oil, grease or heavy coatings of oxide, simple cleaning procedures are often sufficient to prepare the surface from frit undercoating. These may include one or more of the steps of vapor de-greasing, solvent wiping or light compressed air blasting with aluminum oxide, or other fine, clean abrasive powders, or pre-firing the smooth surface to a temperature of 700° F. or more. One or more of these simple cleaning steps is often sufficient to remove light accumulations of oil, grease, oxides or other foreign material.

For highest reliability, however, and to remove heavier accumulations of oxide, oil, grease, dirt or other materials, it has been found desirable and preferable to follow a thorough, three-stage cleaning procedure indicated in FIGURE 6 which is highly effective in preparing rolled aluminum steam iron soleplates for the subsequent stages of the coating processes of this invention.

The first preferred cleaning stage is the immersion of the metal objects in a hot solution of alkaline grease remover for a short period. For example, 5 to 10 minute immersion in a hot solution of a commercial grease remover such as 8 ounces of Oakite No. 164 dissolved in a gallon of water and maintained at a temperature of 160° to 170° F. is sufficient to dissolve and rinse away any accumulations of oil or grease, and this is normally followed by a pressure tap water spray rinse to remove the alkaline bath solution.

The second stage in the preferred cleaning procedure is the immersion of the metal objects for 5 to 10 minutes in a hot solution of a mild pickling acid, a mixture of 20 percent sulfuric acid and 5 percent chromic acid maintained at about 180° F., for example. This mild pickling solution removes any accumulated coating of metal salts or oxides. It may also produce mild, slight etching of the smooth metal surface to be coated, and is again followed by a pressure tap water spray rinse.

Thirdly, the metal objects are preferably immersed in a room temperature solution of mildly alkaline neutralizing salts to provide the final cleaning operation. For example, suitable neutralizing solution contains 1.57 pounds of sodium bichromate, 0.83 pound of sodium hydroxide and 0.021 pound of chromic sulfate, all dissolved in one gallon of water. After 1 to 4 minutes immersion in this neutralizing solution, a final pressure spray tap water rinse prepares the metal objects for the frit coating procedures to follow.

"FRIT" UNDERCOAT FORMULATIONS

The partial, discontinuous "porcelain" undercoating of the metal surface is produced by spraying a "slip" of finely-milled powdered glass "frit" coating material doped with a small inclusion of between about 2 and about 10 percent, and preferably about 4 percent, of powdered "flint" glass, directly on the clean metal surface to be coated. A preferred formulation of the frit coating material includes standard commercial powdered frit materials, pigment and standard hardener in the following proportions:

	Percent
DuPont L–388, frit (100 parts)	55.0
DuPont L-389, mill addition agent (10 parts)	5.5
DuPont K–919, frit pigment (10 parts)	5.5
American Lava Co. No. 1496, frit hardener (10 parts)	5.5
Water (30 parts)	16.5
	88.0

An alternative formulation of powdered frit coating material incorporates Ferro Corporation's finely powdered porcelain undercoat materials, for example:

	Percent
Ferro CN 400 frit (86 parts)	47.3
Ferro AL 6 liquid mill addition (13 parts	7.1
Ferro F 17126 brown pigment (9 parts)	4.9
Water (52 parts)	28.7
	88.0

Since Ferro CN 400 is a mixture composed of Ferro AL–12 frit, a heavy metal-free glass, with other materials, all finely milled and supplied as 200 mesh powder, only thorough blending with the remaining hard-particle frit components and a minimum amount of further milling are required.

The DuPont, American Lava and Ferro frits and additives described above are low-firing temperature silica frits and additives recommended for use on aluminum, and they are proprietary products of E. I. du Pont de Nemours and Co., of Ferro Corporation, or of American Lava Co., and identified in the literature published by those firms in the United States. The chemical compositions are not published by the manufacturers, but these frits and additives are standard, commercially-available products offered for sale and identified in the literature as indicated above.

As indicated in the flow diagram of FIGURE 6, this powdered frit mixture is milled to an average particle size somewhat more coarse than that normally used for the heavy porcelain coating of aluminum sheets for architectural purposes. A suitable fine particle size has been found to be reached when substantially all of the milled "slip" mixture passes through a standard 325-mesh screen.

Following this initial milling, the milled frit is "doped" with a small amount of DuPont RN-505 flint, preferably about 7 parts of 3.8% and 15 additional parts or about 8.2% of water, and the overall mixture of 182 parts total (100%) is remilled to pass again through the 325-mesh screen. The 10 to 1 ratio mixture of DuPont L-388 Frit and DuPont L-389 Agent to provide the principal constituents of the preferred frit mixture has been found to give excellent results when doped with about 4% of "flint" powder. For cooking utensils, lead free frit powders are preferred. Optionally, the 10 parts of DuPont L-389 Mill Addition Agent may be omitted if desired and the following addition agent may be used instead.

Alternative addition agent (10 parts), comprising:

	Parts
Boric acid	2.9
Potassium hydroxide	3.1
Potassium silicate	2.0
Sodium silicate	2.0

UNDERCOATING PROCEDURES

After the fine milling of the flint-doped frit or "slip" mixture is completed, it is sprayed lightly in a fine mist spray over the metal surface to be coated, forming a partial, discontinuous coating. The finely milled powdered frit particles on the metal surface are thinly deposited by the spraying operation in an open, random pattern, where they are held in place by the small amount of included moisture in the frit mixture, as shown in FIGURE 3. Care is observed to avoid "wetting" the metal surface with a thick, flowing mass of the porcelain frit mixture in the manner of applying a coating of paint, lacquer or porcelain enamel. Instead, a very fine, thin discontinuous spray coating generally less than 0.00025 inch thick is applied. Under a microscope, the bare metal surface may be clearly observed between the deposited frit particles, which cover no more than between about 20 to about 70 percent of the metal surface, and preferably about 50 percent of the surface.

As shown in the highly magnified schematic cross-sectional view of FIGURE 3, the standard frit particles **10** are thinly deposited on the metal surface **11**, leaving considerable bare stretches of the surface **11** exposed. The sharp angular flint particles **12** rest upon the other frit particles **10** or directly upon the metal surface **11**, and the particles **11** and **12** are temporarily held in position on surface **11** by the small amounts of about 25% included moisture **13** in the frit sprayed thereon, all as shown in FIGURE 3.

The next step in the coating procedure is the heating of the frit sprayed metal objects to a temperature preferably between 970° F. and 1000° F. to melt the particles of the principal frit ingredients and fuse them as discrete ceramic bodies **10*a*** to the metal surface **11**, as shown in FIGURE 4. Heating at this temperature from 2 to 4 minutes produces highly satisfactory results, with the particles **10** of the principal frit ingredients being fused and firmly bonded as ceramic bodies **10*a*** to the underlying metal surface **11**, as shown in FIGURE 4, while the sharp edged angular particles **12** of "flint" included in the powdered milled frit are apparently not completely fused and bonded to the metal surface **11** to the same degree. Instead, as indicated in FIGURE 4, these sharp angular flint particles **12** may be partially bonded to the surface or imbedded in the fused bodies **10*a*** of the principal frit ingredients, but rather than forming rounded fused mounds **10*a*** of glazed porcelain-type material, the unfused flint particles protrude sharply and angularly from the partially frit-coated surface **11**, as indicated in FIGURE 4.

The frit-undercoated metal surface shown in FIGURE 4, prepared in the manner just described, has a rough, sandpaper-like feel to the touch. Prior to the polymer coating operation, the partially frit-coated metal surface **11** when examined through a magnifying glass or a low-power microscope can be observed to have a multiplicity of disconnected irregular surface bumps **10*a*** of porcelain-like material thereon, and the flint particles, which are generally dark in color, may be observed as separate discrete particles by observation at higher magnifications. The DuPont K-919 frit pigment incorporated in the milled frit is a brown pigment which is used to give the fired ceramic material a color close to the gray-brown color of the primer and cover coats of "Teflon" commonly used in coating cooking utensils. Suitable frit pigments of different colors may be used if desired; for example, gray and green pigments are desired in many applications, and the selection of pigment color is entirely optional.

"TEFLON" COATING PROCEDURES

One or two polymer coatings of such material as the "Teflon" polytetrafluoroethylene materials marketed by Du Pont and other manufacturers are next applied in the conventional manner over the fired discontinous ceramic undercoating.

A single polymer coating is acceptable for many applications, but a double coating of "Teflon" is often preferred for long-wearing performance of the final product. A single coating of "Teflon" is generally about 0.0008 inch in thickness, and a suitable polymer coating for cookware utensils is commonly specified to be between 0.0008 and 0.0012 inch thick. Accordingly the most convenient technique for applying a "Teflon" coating **14** FIGURES 1, 2 and 5 having a thickness falling within this commonly preferred range is a procedure of applying two consecutive coats of "Teflon."

Highly satisfactory "Teflon" coatings **14** have been applied in this manner by first bonding to the partially frit-coated metal surface a coating of 850-319 DuPont "Primer" "Teflon" material, which is sprayed and cured in the surface by heating to a curing temperature between 500° and 600° F., and this is followed by a second coating of DuPont 885-109 "Enamel Teflon" material which is again sprayed and cured by such heating in the usual manner to a temperature between 750° and 775° F., producing an overall "Teflon" coating about 0.0010″ thick.

TESTING THE ADHERENCE OF THE "TEFLON" COATING

Numerous techniques have been prepared for testing the quality of the polymer coating and the strength of its bond to the underlying surface, but generally the most effective test is a simple fingernail or coin scratch test, which should not produce any chipping or peeling of satisfactory "Teflon" coatings. When the coated objects made by the techniques of this invention are subjected to such scratch tests, the abrading object may actually be observed to be polished, presumably by the protruding flint particles which apparently extend at various intervals through the outer surface of the polymer coating, as indicated in FIGURE 5. This tends to confirm the conclusion that the incompletely fused and bonded flint particles may retain their sharp, angular fractured edges protruding through the polymer coating, to provide exposed wear-points or runners on which the coated surface will slide across any underlying supporting object such as a garment being pressed under a "Teflon"-coated steam iron soleplate.

The techniques of this invention are well adapted for the coating of many kinds of metal objects for domestic, commercial and industrial use, and particularly to all types of cooking utensils and pressing devices such as commercial garment pressing units and domestic steam and dry irons, on which the auxiliary soleplates of FIGURE 1 or the permanent soleplates of FIGURE 2 may conveniently be mounted. In making "Teflon"-coated cooking utensils, the constituents of the frit undercoatings are selected to avoid lead compounds or other toxic or heat-deteriorated substances. The auxiliary soleplates of FIGURE 1 may be provided with a peripheral shape and a pattern of steam holes both corresponding with those of the exposed pressing surface of a conventional steam iron, to which the auxiliary soleplate may be bonded by any suitable high temperature-resistant adhesive, such as General Electric Silastic adhesive.

While the objects of the invention are efficiently achieved by the preferred forms of the invention described in the foregonig specification, the invention also includes changes and variations falling within and between the definitions of the following claims.

What is claimed is:

1. An article of manufacture comprising in combination:

(A) a metal object having a smooth external surface overlying a homogeneous internal region of continuous metal;

(B) an intermittent, discontinuous coating of a multiplicity of separate, discrete, independent bodies of ceramic material fused to the external metal surface incorporating a minor proportion of between about 2% and about 10% of particles of unfused flint glass; and,

(C) a coating of at least one layer of polytetrafluoroethylene overlying the metal surface and surrounding the major proportion of the overall height of the bodies of fused ceramic coating material thereon.

2. The article of manufacture defined in claim **1** wherein the metal object is a plate configured to form the soleplate of a domestic pressing iron.

3. The article of manufacture defined in claim **2** wherein the metal plate is provided with a periphery shaped to conform to that of a domestic steam iron and is provided with steam passage aperture means passing therethrough for communication with corresponding steam passage means in the underside of the steam iron.

4. The article of manufacture defined in claim **3** wherein the metal plate is provided with a smooth uncoated back surface for adhesive bonding to the underside pressing surface of a steam iron, with its aperture means positioned in registration with the corresponding steam passage means in the underside of the steam iron.

5. The method of manufacturing metal objects having polymer-coated surfaces comprising in combination the steps of:

(A) cleaning each metal object's surface to be coated;

(B) applying in a thin, discontinuous coating to the cleaned metal surface a finely milled ceramic "frit" coating material incorporating between 2% and 10% by weight of powdered flint coating material and a minor proportion of water;

(C) heating the metal objects with the frit coating thereon to a temperature between 970° and 1000° F. to fuse the ceramic frit into a discontinuous coating on the cleaned metal surface comprising a multiplicity of separate, discrete bodies of ceramic materials fused thereon and having particles of unfused flint coating material protruding therefrom, and

(D) applying at least one layer of polytetrafluoroethylene coating material to the metal surface, substantially surrounding and imbedding the bodies of fused ceramic material in the polytetrafluoroethylene coating material.

6. The method defined in claim **5** wherein the flint constitutes about 4% of the powdered frit coating material.

7. The method defined in claim **5** wherein the ceramic frit coating material is finely milled before the addition of the flint to pass through a 325-mesh screen, and is finely milled after the addition of the flint to pass again through a 325-mesh screen.

8. The method defined in claim **5** wherein the fused frit coating material covers about 50% of the cleaned metal surface.

9. The method defined in claim **5** wherein each metal object's surface to be coated is immersed in an alkaline solution and also in an acid pickling solution during the cleaning thereof.

10. The method defined in claim **5** wherein the finely-milled ceramic frit coating material includes the following constituents in these approximate weight percentages:

	Percent
Finely powdered frit materials	60.5
Frit pigment	5.5
Frit hardener	5.5
Finely powdered flint glass particles	3.8
Water	24.7

11. An article of manufacture comprising in combination:

(A) a metal object having a smooth external surface overlying a homogeneous internal region of continuous metal;

(B) an intermittent, discontinuous coating of a multiplicity of separate, discrete, independent bodies of ceramic material incorporating a minor proportion of between about 2% and about 10% of relatively hard sharp-edged unfused protruding flint glass particles, said ceramic bodies being fused to the external metal surface; and

(C) a coating of at least one layer of polytetrafluoroethylene overlying the metal surface and surrounding the major proportion of the overall height of the bodies of fused ceramic coating material thereon.

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RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

38—97; 117—70, 75, 104, 132