My invention relates to a method of coating the surfaces of articles with composite materials by electrodeposition and also to a method of producing electroformed structures by the electrodeposition of such materials.

The principal object of my invention is to provide an economical method of producing electroformed structures and electroplated coatings of mixed materials which will have superior resistance to wear, abrasion, erosion, corrosion, heat, galling and impact.

A further object is to provide a practical method for the electrodeposition of metals with certain solid additives in comminuted form which can be included singly or in combination and which can be of such insoluble materials as oxides, carbides, diamonds, metallics, ceramics or other minerals.

Another object is to economically produce new materials, with nonextant properties, through electrochemistry.

Furthermore, it is an object to effect a new method for the electrodeposition of composite resistant coating materials on the surfaces of tools, dies, punches, gauges and other implements of fabrication as well as fabricated parts and assemblies such as aircraft propellers, turbine buckets, aircraft and missile skin surfaces, combustion chambers, valve seats, piston rings, cylinders and other articles.

Still another object is to provide a new method for the electrodeposition of composite, resistant materials on removable or soluble master forms to produce structures such as molds, female thread ring gauges, plain ring gauges, cylinders, dies and other fabricated items.

A further object is to conserve strategic and expensive materials through the combination of certain abundant solid additives with electrodeposited metals.

Moreover, it is an object to provide an economical and practical method whereby certain solid additives of comminuted form are recirculated through the electrolyte and are electro-codeposited with the metal to form coatings or structures.

Furthermore, an object is to provide a method for controlling the concentration and distribution of solid additives while they are recirculated through the electrolyte and electro-codeposited.

The use of my process for producing composite materials for coatings or structures through electrodeposition, permits a combination of a wide range of materials while allowing ease of control as well as low cost for suitable production equipment. The use of certain solid additives also permits a high rate of composite material deposition.

In the following description and in the claims when I refer to the resistant coating I mean the composite coating of metal and of additives which are resistant to wear, heat and corrosion, and when I refer to the backing layer, I mean the coating of corrosion and/or stress-free metal.

In carrying out my method as applied to electroplating, when for instance the skin surfaces of aircrafts or missiles are to be provided with a heat, wear and corrosion resistant coating, the article must be thoroughly cleaned and dipped into the electrolyte of the plating bath before oxidation can occur. The desired solid additives are mixed

with the electrolyte of the bath and the same is circulated through the bath by suitable pump means. The article after being placed within the bath is preferably agitated or rotated, and a resistant composite coating of metal, such as chrome or nickel and additives is codeposited by electroplating upon said surface. The grains of the additives being in suspension in the electrolyte are brought into contact with the surface being treated and are bonded together and to the surface by the electrodeposition of the metal being deposited from the electrolyte used. If it appears wise or necessary to protect the surface of the article against corrosion or impactive cushioning before the resistant coating is applied, the article may be placed in an electroplating bath and a backing layer of stress-free metal applied to the same before the resistant coating is deposited thereon.

As an illustration, when my method is used to coat the interior of an aluminum rocket combustion chamber where the gas temperature may reach approximately 5000°F., I use hard nickel and deposit a resistant coating of approximately 0.002 inches thick with a concentration of silicon carbide as an additive of approximately 35% by volume.

When my invention is applied to electroforming, a suitable master or matrix as a counterpart of the article is first accurately made. This master is properly cleaned and then placed in an electroplating bath having the electrolyte thereof charged with the desired additive, and a coating of the selected metal and additives deposited upon the surface of the master to the desired thickness. When electroforming by

means of my method, it is desirable that a backing layer of stress-free metal be deposited upon the resistant coating so as to reinforce the latter. When electroforming or electroplating, it is desirable that the master or the article be rotated or agitated, and the rate of rotation or agitation thereof plus the specific gravity of the electrolyte, the specific gravity and concentration of the additives in the electrolyte, and the current density will determine the concentration and distribution of the additives and the rate of the deposition.

In the accompanying drawings, I have shown a number of illustrative embodiments of my invention and an illustrative apparatus for carrying it out.

Fig. 1 illustrates a fragmentary sectional view of the surface of any object such as an airplane propeller or wing, or the surface of a rocket combustion chamber which has received and electrodeposited resistant coating by my method;

Fig. 2 is a fragmentary sectional view of a modification of the invention shown in Fig. 1;

Fig. 3 is a side elevation of a master for use in making an electroformed thread gauge by means of my invention;

Fig. 4 is a sectional view of the master with a resistant coating deposited thereon;

Fig. 5 is a similar view with a backing layer electroplated upon the resistant coating and the outside diameter machined;

Fig. 6 is a fragmentary sectional view of a backing layer formed by continuing the plating of the resistant coating with additives until the desired thickness has been reached;

Fig. 7 is a view of the finished article with the master removed;

Fig. 8 is an enlarged fragmentary view of the finished thread gauge;

Fig. 9 is a sectional view of a ring gauge made by my method;

Fig. 10 is a sectional view of a pair of dies made by my method; and

Fig. 11 is a schematic view of an apparatus for carrying out my method.

In this application, I have shown my invention as applied to electroplating of the surfaces of articles of manufacture and also to the electroforming of articles, and reference is to be had to a co-pending application upon Electroforming.

Referring to Fig. 1 where I show my invention as applied to the treatment of the surface of an article, 15 represents the fragmentary cross sectional portion of an airplane wing, propeller, a rocket combustion chamber, or the like. The composite electrodeposited coating material consisting of the suitable metal and additives is represented at 16. The metal deposited may be nickel, chrome, copper, cadmium, etc., and the additives which are in comminuted form may consist of oxides such as aluminum and iron oxides, carbides such as tungsten and silicon carbides, diamonds, metals and the like, or a suitable mixture of any of these materials which will produce surfaces with extremely good wearing qualities, hardness, lubricity and/or resistance to corrosion, heat an erosion. Additives of conductive material serve to increase

the rate of material deposit, thereby reducing the cost of applying the resistant layer. The surface 20 of the article is, therefore, protected against wear and erosion, as well as very high temperature. In the event that an undercoating of stress-free metal is desired, a backing layer 21 (shown in Fig. 2) is applied to the surface 20 of the article before the resistant coating is deposited thereon.

In carrying out my process in the making of the illustrative thread gauge 23, shown in Fig. 7 by electroforming, I first prepare a master 24 (shown in Fig. 3), of which the finished gauge is to be a counterpart, of material soluble in acid or alkali; as for instance of hard aluminum or any other suitable material. While this master may be of solid material, it is obvious that in the interest of economy, it may be hollow and formed with a recess 25. A mask 32 is placed at each end of the master to prevent electrodeposition. A resistant composite coating 26 of hard metal such as chrome, nickle or the like, containing additives 27, is first plated upon the master in a primary electroplating bath. This is shown in Fig. 4. After completing the plating of the resistant coating, the master is removed from the primary electroplating bath and placed into a secondary plating bath where a backing layer 30 of stress-free metal is applied, as shown in Fig. 5. The backing layer may contain additives since by using additives with a thermally compatible metal such as nickel, the rate of deposition will be increased and the cost of material will be decreased without any sacrifice to the stress-free characteristic of the back up layer. If desired, the plating may be continued in the primary bath with additives to form the backing layer 29 as shown in Fig. 6.

After the backing layer is of the desired thickness, the article is removed from the bath and preferably placed in a lathe and turned down so as to provide an exterior surface 31. A heat insulating sleeve 38 is placed over the surface 31 to protect the gauge against temperature changes when being used. The unwanted master which is exposed by the removal of the masks 32 is removed by dissolution with acid or alkali leaving in this instance the smooth acid resistant coating 26 having the exact counterpart of dimensions and surface characteristics of the carefully formed master.

In electroforming the ring gauge 11 shown in Fig. 9 of the drawings, I proceed in substantitally the same manner as that above described in connection with the thread gauge. A master or replica (not shown) having the same diameter as the article to be measured by the gauge is first made, after which the resistant coating 33 containing the additives, hereinbefore mentioned, is applied to the master. The master with its resistant coating is then transferred to a secondary electroplating bath (not shown) and a backing layer 34 applied on top of the resistant coating. The coatings (not shown) over the ends of the gauge and master are then removed in a manner similar to that above described, and the coatings together with the master are immersed in a bath to chemically dissolve the master. After the exterior of the backing layer has been turned in a lathe, as hereinbefore described in connection with the thread gauge, the gauge is provided with a relatively smooth cylindrical surface 35 upon which a protecting sleeve 37 of heat insulating material is placed.

In forming the parts of the die shown in Fig. 10 by my method, a master 31 is made of suitable material, and the upper and lower dies 40 and 41, respectively, are provided on the working surfaces with an electrodeposited resistant coating 42 containing suitable additives, after which the parts are provided with backing layers 43 and 44, respectively, which are later machined to adapt them for use in a suitable stamping press or the like. This backing layer may be formed in the primary electroplating bath with or without additives, as in the case of the gauge, or it may be transferred at this stage to a secondary electroplating bath (not shown). When the master does not have reentrant portions the die parts may be mechanically separated. If reentrant portions do exist the master will be removed by dissolution. When electroplating the die parts it is preferable to mask a portion of the periphery of the master, as shown at 45 in Fig. 10, so as to facilitate mechanical separation of the parts or to make the master accessible to the solvent if dissolution is necessary.

Instead of suspending the additive grains, the resistant coating may be applied directly to the master by spraying, dipping, or brushing. In this case the resistant grains are mixed with a suitable adhesive liquid such as a lacquer and applied to the master, in the desired thickness, and allowed to dry. Metallic paints, such as silver, when properly mixed with the resistant additive grains, are excellent for this method of applying a resistant coat to masters made from nonconductive materials. The coated master is then immersed in the plating solution and the

desired thickness of metal is electrodeposited thereon and through the interstices of the applied grain coating to bond the same. When the master is then dissolved or mechanically stripped, the coating, which becomes bonded by the electrodeposited metal, presents a smooth, highly resistant surface. In some applications where characteristics other than resistance are required, other particles, such as graphite, can be used in the place of, or combined with the resistant particles mentioned, to produce anti-friction surfaces. Highly precision sleeve bearings are a good example for this type of application.

Referring to Fig. 11 where I show an illustration of an apparatus suitable for carrying out my invention, 46 represents the electroplating bath having an electrolyte 50 containing dissolved therein a cation suitable for the metal to be deposited and containing the proper additives 47 for the desired coating. The anodes 51 are preferably disposed at opposite sides of the bath and are supplied with electric current in the well known manner and of voltage and amperage proper for the metal being deposited all as is well known in the art of electrodeposition. The article illustrated at 52 is arranged preferably between the anodes 51 and is properly prepared to act as a cathode and to receive the electrodeposited metal from the electrolyte and additives suspended therein. In carrying out my method, it is preferable that the article be rotated or agitated so as to facilitate uniform deposits of the metal and the included additives.

So as to keep the additives in suspension and readily applicable to the surface of the article, the electrolyte 50 is preferably circulated by means of a pump 53 which draws the electrolyte and additives through a manifold inlet 54, arranged across the bottom of the tank and directs it into a screening unit 55 by means of a pipe 60. The screened electrolyte with the additives are returned to the bath by means of a pipe 60. The additives are thus precipitated into the article 52, and are then codeposited with the metal to form a composite coating material. A valve 61 is preferably provided in the return pipe 60 whereby the amount of additives used may be regulated or shut off entirely in cases where the electroplating of the backing layer without additives is to be done in the same bath. It is obvious that the apparatus is applicable in carrying out my invention as applied to electroplating or electroforming.

As indicated above the additives used in carrying out my method may be water insoluble inorganic salts, metallic oxides, metallic carbides, metallic carbonates, so-called abrasive grains or finely divided metal and should be insoluble in the electrolyte. These additives can be of a size covering substantially the entire range of United States Standard sieve sizes ranging from number 10 to number 1000 or finer. However, a size corresponding to the United States Standard number 600 and upward will be suitable for most applications. The percentage of additive by volume in relation to the codeposited metal depends upon the characteristic required of the finished resistant coating and may be any where from 1% to 90% by volume.

From the foregoing it will be obvious that when my method is employed in the manufacture of articles of fabrication, the life of the article is greatly increased and the accuracy thereof is maintained over long periods of service. As an illustration, my invention was used to treat the surface of a punch used in a hot punch press in the manufacture of automobile engine poppet valves. This punch was electroplated with a composite coating of nickel and silicon carbide of number 1000 grain size. This coating was .0007 inches in thickness with a 50% concentration of additives by volume. In actual working conditions this punch produced 787 workpieces whereas the punch not treated by my method, operating under the same working conditions, produced only 248 workpieces before having to be replaced, thereby showing a greatly increased working life of the punch. However, in the above use of the invention aluminum oxide may be substituted for the silicon carbide or used in combination therewith.