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METAL PLATING

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Fig. 1.

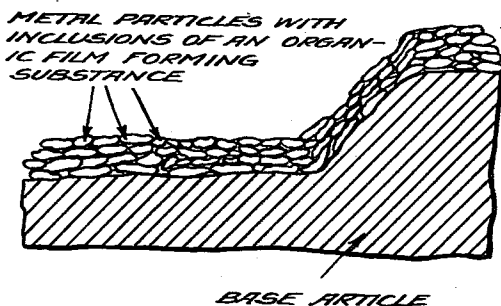
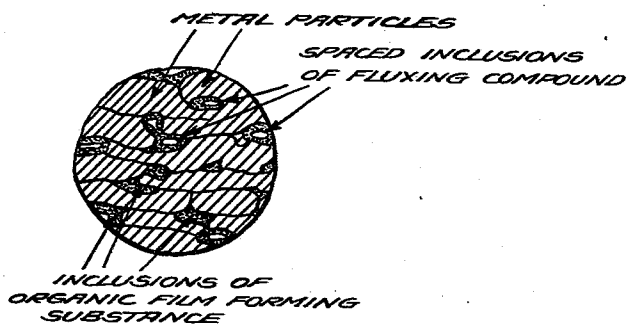


Fig. 2.



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3,132,043

METAL PLATING

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 Continuation of application Ser. No. 670,355, May 27, 1957, which is a continuation of applications Ser. No. 99,567, June 16, 1949, and Ser. No. 3,537, Jan. 21, 1948. This application Mar. 25, 1963, Ser. No. 267,854
 10 Claims. (Cl. 117-109)

This invention relates to metal coatings and particularly to such coatings progressively built up to desired thickness on a base surface of metal or other material. This application is a continuation of my application Serial No. 670,355, filed May 27, 1957, now abandoned, which is a continuation of my application Serial No. 99,567, filed June 16, 1949 which, in turn, is a continuation-in-part of my application Serial No. 3,537, filed January 21, 1948, now Patent 2,640,001, issued May 26, 1953, and application Serial No. 14,639, filed March 12, 1948, and Serial No. 77,269, filed February 18, 1949, both now abandoned.

An object of the invention is to provide a coating which will be inexpensive in application, attractive in appearance and effectively adherent to the base surface and protective against weather, wear and corrosion.

To attain this structure a composite coating is built up of macroscopic solid particles of the coating metal deposited on the base surface and brought into surface-to-surface contact and adhesion therewith and overlaid with continued similar deposits of said particles inter-fitted in metal to metal contact and cohesion into a solid surface covering of desired depth.

Further objects of the invention, particularly in the method of applying the coating to metal and other surfaces without application of electric current or melting heat, will appear from the following specification and the accompanying drawing forming a part thereof, wherein:

FIG. 1 is a representative cross-section of a metal coating embodying my invention, and

FIG. 2 is a portion of the cross-section at great magnification.

Referring to a typical embodiment of the invention as shown in FIG. 1, a coating of clean metal particles, for example zinc, is applied to a base article, for example steel, the under surface of the coating being formed of zinc particles brought to the base surface and adhered thereto by sufficiently concentrated pressure to give a metal-to-metal contact developing interatomic attractive forces between the metals. This initial or bottom layer of particles covers the entire coated area continuously, each particle being individually attached to the steel surface by adhesion, the adhesive forces brought into play by the physical metal-to-metal contact of clean surfaces joined together by pressure and locally generated heat. Mechanical bonding of the particles into the "tooth" or surface irregularities of the base may play a part in the attachment of the coating, but it is believed that the main forces concerned in the weldment are molecular or atomic in nature and involve Van der Waals forces, covalent bonds, metallic linkages and ionic bonds. All of these forces can exist when a second metal atom is introduced into an assemblage of other metal atoms.

The coating metal particles as fixed in place are preferably small, .5 to 20 microns in largest dimension, for example, and are pressed against the steel surface by blows of heavier pieces such as whole or cracked steel shot so that the particles in position on the steel surface are impacted by the heavier pieces into such close metal-to-metal contact with the steel that a permanent bond is formed securing each particle in place. This impacting of the zinc particles tends to flatten them in

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the direction of the base surface extending the area of contact and the opposite area of the particle subjected to the blows.

For instance, particles of zinc dust intermixed in a fluid medium with heavier particles and the articles to be coated may be treated in a tumbling barrel provided with peripheral riser bars and rotating on its axis to stir and lift material and drop it back onto the charge at the bottom, as set forth in my copending applications above referred to. Or the coating may be built up of colloidal particles rubbed off from zinc coated shot and impacted in interfitting engagement to form the protective layer.

I have found that it is of critical importance to the strength of the bond that a most intimate metal-to-metal contact should be attained over the interengaging area of each particle and the base surface. Oxide films and other films of inorganic salts of the metals, and many other compounds, weaken or prevent adhesion, and must be avoided or removed from between the surfaces to permit the metals to adhere. Such films may be reduced or removed mechanically by attrition or chemically by fluxes or both, it being important as the depositing operation progresses to prevent or retard reforming of any weakening or corrosive film on the surfaces of the particles.

It will thus be seen that there are two things done to establish the best coating. The result is, as shown in FIG. 2, an inclusion throughout the coating of an organic substance forming a film over the unbonded clean surface areas of the particles. There may also be present inclusions of a fluxing compound, or reaction products thereof, spaced from the clean metal particle surfaces by the organic film.

The flux is used to remove oxides and other contaminating films from the metal particles and the surface to be coated, and the film forming material is used to film the clean surface of the metal particles and the surface to be coated and protect them until the weldment of the particles to the surface is accomplished and at which time the film forming material is positioned in interstices in the coating.

These two functions are separate and distinct even though both of them may be confined to the use of a single filming material which acts both as a flux and as a film former.

Fluxes should not be confused with or compared to film formers as no flux of the prior art serves both functions but the film former may serve both functions. On the contrary, however, there are film formers which are acid or alkali in character and oily and film forming and thus combine in one material both functions. Even though both functions are concentrated in one material they are both equally desirable to obtain the best coating. The fluxing operation can be aided by mechanical scrubbing if the plating operation is carried on in an environment where reoxidation of the metal is reduced to a minimum.

An important difference between the flux and the filming material is that the flux is not sticky, while the surface active filming material is not only sticky but adheres most strongly to clean metal so that it is retained in the interstices of the coating where it does exert a definite protective and beneficial effect.

The filming material, because of its sticky and adherent nature, is thus retained in the coating in much larger traces than the reaction products of the flux.

In those cases where only a flux such as disclosed in the prior art is retained in the coating, the effects are all harmful on its life and usefulness. Such flux or other contaminating material acts to reduce the thickness and strength and adhesion of the coating and to increase its porosity and further reduce the useful life.

Where corrosive fluxes are used, such as zinc or am-

monium chloride, the harmful effects of such retention of such inclusions of flux in the coating are greatly magnified and cause a bloom and actual disintegration of the coating in time rendering it commercially impractical.

An effective procedure mixes the articles such as steel bolts, nuts and the like with the zinc dust or powder and steel shot in a tumbling container preferably sealed to exclude air. In this case aqueous or other liquid suspending medium is omitted. The tumbling of the container subjects the articles to direct contact with the zinc particles under conditions of rubbing, attrition and impact removing or penetrating surface films and bonding the metal surfaces together. The exclusion of oxygen tends to avoid recurrence of oxide films and the clear metal surfaces of the zinc particles become attached directly to the metal of the articles accumulating and confirming the particles as a covering base layer of zinc grains having strong adhesion to the steel and strong cohesion to each other at their areas of contact. Upon this adhering base layer the continued tumbling of the dry mixture deposits and attaches the zinc particles by their clear surfaces giving strong zinc-to-zinc bonding and rapidly building up the assembled coating to desired thickness with the flattened particles interfitted and overlapping and generally parallel to the base surface.

This "dry" attaching and impacting of each small powder particle concentrates and intensifies the applied pressures to give a very intimate union of the metal surfaces developing bonding forces of great strength brought into play by the union of the clean metal surfaces under the pressures and heat generated by the mechanical forces used to distort the particles. These forces appear to involve combination of one or more of the following forces: Van der Waals forces; covalent bonds; metallic linkages; and ionic bonds. The slight inclusions of removed oxides are negligible and substantially undetectable and there are no intervening films or deposits from a suspending liquid. The intensified bonding action adapted to this procedure to a variety of metal coatings and at room temperature is effective with aluminum as well as the softer zinc, cadmium, lead and tin giving relatively thick deposits, for instance .006", in short times of treatment.

With the metal particles thus surface-worked in the tumbling or other operation, the particle surfaces develop a high free energy because of the decrease in the volume of the strain free matrix which in the resultant intimate metal-to-metal contact with each other at the areas of interfitting there appears to be some recrystallization which in some cases merges across grain boundaries. Some particle apparently grow rapidly in size with resulting grain growth across the particle boundaries so that individual smaller particles amalgamate into larger grains. Enlarged crystals of continuous dense metal apparently develop by recrystallization involving the amalgamation of a number of particles originally present in the coating to form large grains. It is also true that some recrystallization may occur within the individual boundaries of a particular particle, both types probably proceeding together.

Where, as with processes employing a liquid suspension of the metal particles, there is a wetting film initially present between the particles at the areas of interfitting, the impacting thins this film and displaces it except for the residue retained chemically as in the case of ionic solutions particularly of reactive inorganic salts promoting couples between dissimilar surfaces and developing high solution pressures increasing in current effect with the close approach of the particles. Such chemically retained residues intervening especially between the coating and the base metal prevent or reduce metal-to-metal contact there and appear to reduce the cohesion of particle-to-particle.

With films of other suspending liquids, however, such as those merely inhibiting oxidation, the compacting of

the particles reduces and removes them to a degree causing the films to part between the interfitting metal surfaces so that the cohesive forces of metal-to-metal contact are accompanied and increased by recrystallization across the boundaries. We then, under such conditions, have areas of metal-to-metal bonding interspersed with areas of intervening thin film formations and secondary valence bonds are available to aid in holding the surfaces together in contrast with the reactive inclusions which intervene and weaken and eventually corrode the bonding areas. The building up of the coating of this invention thus provides intimate metal-to-metal bonding with incident recrystallization across the boundaries or at other points a random bonding with incident recrystallization across the boundaries or at still other points combines this with a random mixture of such bonding with film attraction of the surfaces by secondary valence bonds, this latter combination resulting where there is employment of liquid suspensions for the metal particles. It is important that this liquid act to inhibit oxidation and it is also advantageous to combine with this a surface-active effect wetting the surfaces of the particles and the base metal in a manner tending to develop adhesion between them. By referring to the surface-active effect, it is that class of organic material capable of exhausting itself on clean metal and other surfaces as a thin molecular film, said film acting to coat and protect. The film forming substances that are in the interstices of the coating have this surface-active effect. The particles are thus massed together into a unitary structure by the secondary valence bonds of the intervening films of an oxidation inhibitor and by recrystallization across the interfitting surfaces of said particles, said recrystallization penetrating and interrupting said intervening films.

I have found that aliphatic carboxylic compounds of the class belonging to fatty acids and their derivatives possess very desirable characteristics in connection with the liquid suspension of the metal particles for plating. Of these compounds a substituted ammonia compound is particularly efficacious. For example, if R represent the carbon chain corresponding to the fatty acid, then the primary amine is RNH_2 in which one of the hydrogen ions of the ammonia has been replaced with an alkyl radical. Where two or three of the hydrogen ions are replaced, the amine becomes a secondary or tertiary amine respectively. In the plating of some metals, it is sometimes an advantage to substitute an organic alkali such as the amines just discussed for the fatty acids, as they are less reactive and cause less gassing in the mill. In some types of mix, the use of fatty acid causes formation of substantial amounts of metal soaps which may thicken the liquid to the point where good plating is impaired. The use of the organic alkali eliminates the formation of this type of soap.

A preferred primary amine is one derived from a soya base and has the following approximate composition: Hexadecyl, 10 percent; octadecyl, 10 percent; octadecenyl, 35 percent and octadecadienyl, 45 percent. A tertiary amine derived from this primary amine is obtained by condensing ethylene oxide with the primary amine.

Since the amines are alkaline, they may be reacted with other fatty acids or with organic or inorganic acids to produce neutral salts. Some of these salts, for example the amine acetate formed by reacting the amine with acetic acid, have the desired characteristics for plating.

The amides are another type of aliphatic carboxylic derivative which produce satisfactory results. The primary amide as used in my method is defined as the derivative of an organic acid in which an amine group replaces the OH group. Therefore, using R as before, a primary amide is $RCONH_2$. Secondary and tertiary amides are also effective. Both the fatty acids above six carbons in chain length, and the fatty derivatives just discussed, are instances of oily sticky film forming compounds that have

the property of exhausting themselves on the surfaces of the metal dusts used in coating, and on the surfaces of the articles to be coated. Fatty acids have a strong solvent action on metal oxides. These oxides that exist on the surfaces of metal particles of a fine metal dust are extremely thin and are thus readily dissolved in the form of metal soaps by the fatty acid, or are attacked by an organic acid or weak alkali such as those previously mentioned.

While not wishing to be limited to any theory as to the surprising fact that any oily film forming material promotes the welding or joining of metal surfaces, it appears that the film forming material may not attach itself to an oxidized surface, or attaches itself less strongly. In the latter case it is more apt to be removed by the abrasive forces involved in the tumbling or agitating operation, thereby exposing the oxide to attack by abrasion and by any organic acid or weak alkali present. The fatty acid film formers will directly attack and dissolve oxides as soaps.

After this oxide film has been removed from the surface of the particle, the oily film former reforms on the clean metal and adheres tightly, thereby shielding it not only from further chemical attack, but also from reoxidation by air, water, or from its environment. Further, the very thin sticky film may serve as a means for temporarily joining the surfaces together before they are welded by the applied mechanical forces. The increase in surface area of the particle after it has been flattened, creates clean new metal. The increase in surface area is believed to fracture the film which is believed to be of mono molecular thickness and clean metal-to-metal contact of the mating surfaces is thereby secured and welding results. Subsequent impacts then squeeze out most or all residual traces of film former which thus has a tendency to collect at the boundaries of the particle and become entrapped in the coating as inclusion in microscopic amount. These inclusions are also highly beneficial as a holding aid and in conferring tarnish resistance to the coating, and show in the figures as the approximately round black areas concentrated particularly at the boundaries or unbonded surfaces of the grains or particles. These round dark spots appear occasionally in the interior of the larger masses and are believed to have been left by recrystallization across grain boundaries. When a particle is flattened by the sudden drastic impact, the work done on it raises its energy level substantially and imparts considerable atomic mobility to the disarranged atoms in the particle. Succeeding impacts, it is thought, actually cause recrystallization to occur between particles. This recrystallization occurs during the process and not after the process is completed. Hence, it is not intended to imply that the material exists in an annealed state.

Normal recrystallization processes produce an annealed condition with equiaxed grains, but in the instant process the fact that recrystallization occurs under stress results in deformation in a preferential manner.

When using the amine or amine salt in the carrying or tumbling liquid during the plating process, the mill can be operated indefinitely at a satisfactory plating efficiency without the necessity of removing the powder and the liquid for washing and purification. Fresh metal dust must continually be added to replace that plated on the objects. It is also necessary to add fresh amine from time to time, as well as further carrier liquid to replace that lost in dragout on the objects removed. If desired, the dragout liquid may be recovered by washing, distillation or other means, and returned to the mill for reuse.

In addition to being organic alkalies, the amines are also emulsifying agents. Furthermore, they are cationic wetting agents and render the surfaces of the metal flakes water rejecting and oil accepting surfaces. Consequently, by taking advantage of this property, I can use plain water in lieu of the organic solvents set forth above as a major ingredient of my tumbling media. While the

organic solvents are suitable in some instances, particularly due to their expense, inflammability and their toxicity, they are sometimes less desirable than plain water.

Therefore, by using amines in water as cationic wetting agents either alone or in combination with a water soluble oil the metal being processed, zinc for example, is coated with lubricant and satisfactory plating will result.

The amines may be reacted chemically to produce other very suitable compounds for use with water as a plating fluid. For example, fatty acids may be reacted to form water soluble nonionic surface active agents, the fatty acid amines may be condensed in ethylene oxide to produce water soluble cationic wetting agents.

These oily film forming detergent materials act to coat the particles of metal and the metal surfaces, and to shield them from reoxidation once they have been cleaned. Many of them are powerful detergents and aid in removal of oxide. Others, such as the fatty acids, for example, have chemical oxide solvent properties of their own, and thus also aid in cleaning the particles of oxide. The film-forming material thus may act in one or more of several capacities: either as a physical film which acts as a barrier between the metal particles and further corrosion by oxygen; or as a chemical solvent for oxides; or as a detergent or cleansing agent. Cationic and non-ionic wetting agents, detergents, oils and gums, are useful in promoting the coating. Specific examples of materials suitable for use with water are the water soluble glycols such as ethylene glycol or a cellulose gum material such as carboxymethyl cellulose used with ammonia or other alkali cleanser.

When high temperatures are necessary, special carrier organic liquids capable of withstanding heats up to 250 degrees centigrade or higher must be used. Organic liquids that have been found suitable include certain processed whale oils, some organic phosphates and some of the glycols. Some of the saturated fatty acids, such as stearic, may be used alone as both the carrier liquid and the plating agent, because at high temperatures these materials form thin liquids. In the plating of metals whose recrystallization temperatures involve heats in excess of approximately 300 degrees centigrade, organic liquids cannot be used and it is necessary to use fused salts as the carrier liquid.

The choice of the chemicals for plating depends on the type and character of the objects to be plated, the kind of metal it is desired to plate, and thickness of the coating desired, as well as its brightness and smoothness, and the speed at which it is to be deposited. Taking zinc by way of example, it may be plated satisfactorily in water using one of the water plating agents just discussed. This will give smooth thick bright coatings. Zinc may be plated equally well in nonaqueous systems at elevated temperatures using whale oil, tin fat, tributyl stearate or other suitable carrier liquids such as those described. Alternatively, it may be plated from a continuously operating bath at temperatures somewhat above room (60 degrees centigrade or thereabouts). At this temperature kerosene or high-flash naphtha may be utilized with a suitable plating agent, such as one of the fatty acids. Zinc may also be plated very well at room temperature from a continuously operating bath using a volatile solvent such as alcohol, xylene, benzene where a fatty amine is added as the plating or active principle. Not all metals may be plated in all of these ways. Copper and silver, for example, must be deposited at elevated temperatures.

In the nonaqueous field, some of the surface active agents found useful in promoting plating include the vegetable and marine oils and the fatty acids derived from them, such as oleic, linoleic, cluponadonic, caprylic, capric, myristic, palmitic and stearic—to name a few of those specially suitable. In particular, the distilled fatty acids from linseed or soya oils are very efficacious. It is rather remarkable that an oil or fatty acid which is an extremely slippery lubricating material should be effective in

applying a metallic coating to a metal object. On the face of it, it would appear that if it were desired to apply a metal coating by hammering or rolling with small balls, the last thing for use to accomplish this end would be a lubricating oil.

For successful metal plating in the tumbling mill, it has been found that the volume of liquid to metal powder is extremely important. A large range is permissible and different effects result where the quantity of liquid used is small and where the liquid to metal ratio is large. If too little liquid is used, the mixture is pasty. The material may then pack loosely around the article being plated and it is then shielded from further action; on the other hand, if a large excess of liquid is used, the coating time is increased and the metal deposited on the articles tends to be thinner and brighter.

Where no balls are used, the small objects being plated serve the same purpose as balls. In other words, when plating a charge of small wood screws, for example, these screws are adapted to take the place of balls. This would simplify the process in that it would not be necessary to separate the screws or other small objects from any steel balls and the screws or other small objects would be very nearly as effective.

The use of small balls is especially advantageous in the plating of irregular shaped objects having exterior and interior surfaces inaccessible with large balls of the size customarily employed in ball mills. By using shot or small balls a good coating of such irregular shaped objects, both exteriorly and interiorly thereof, is effected. In place of round balls, crushed iron and shot may be used, the sharp broken corners of this type of material assists in reaching into recessed areas that may not be reached even by very small round shot. In lieu of the crushed shot, other broken or sharp pointed pieces of iron may be substituted where it is desired to plate to the bottom of threads or under nail heads or other similarly secluded areas. Materials of this sort which are suitable are: small brads and nails, tacks, nail whiskers, burnishing needles and cones. Care must be taken in selecting the size and character of the grit used to prevent it getting caught in recesses such as the slot on the head of wood screws.

The temperature at which plating is done depends on the metal being plated. It is necessary to operate within the minimum recrystallization temperature range for drastically cold-worked metals. In the case of metals such as zinc, tin and lead which recrystallize at or below room temperature, the plating may advantageously be done at room temperature. There is no disadvantage, however, to plating these metals at higher temperatures. The operation at more elevated temperatures tends to promote more rapid build-up of the coat and greater adherence. The recrystallization temperatures of other metals ranges on up and is 150 degrees centigrade for aluminum, 200 degrees centigrade for copper and silver, 450 degrees centigrade for nickel etc. Heat generated at the point of impacts may be sufficient to raise the temperature locally to the minimum for recrystallization, and thereby secure plating even when the general temperature of the bath is below the recrystallization temperature.

It has also been found more satisfactory to exclude air from the interior of the mill and operate with the mill sealed. The exclusion of air is not necessary for plating, but is highly desirable and permits bright metal plating.

The small steel shot or balls serve to hammer the metal on the objects being plated. The finished object looks as if it had been electrolytically deposited and then buffed or polished. The coating is completely adherent and will not rub or wash off or break or fracture under various strains and flexures.

In another effective procedure, the articles to be plated are placed in a ball mill containing a carrying or tumbling liquid which consists of a mixture of a volatile solvent and a saturated or unsaturated fatty acid. This acid may be

derived from fats, tallow, vegetable, marine or organic oils as, for instance, linoleic acid, linolenic acid, oleic acid, caprylic acid and especially suitable are those derived from rapeseed, flaxseed and soya beans. In general, any of the fatty acids may be utilized.

The solvent may consist of mineral spirits or any volatile organic liquid such as toluol, xylol, hydrocarbon naphthas, chlorinated hydrocarbons, glycol ethers, alcohols (ethyl, butyl and isopropyl) and ketones (di-isopropyl ketones).

The mill is then charged with a quantity of small steel balls approximately $\frac{1}{16}$ inch to one inch in diameter. Then, finely powdered dust of the metal or metals to be plated, zinc for example, is added. The mill is then closed and rotated and a bright metallic zinc coating is hammered or impacted onto the articles providing a very smooth, dense, lustrous coating. When the articles are examined under a microscope, it is found that a solid layer of metallic zinc has been built up thereon.

No heat is necessary in this method, the impact of the steel balls hammering the finely divided metal into chemically clean flake form and plating the same upon the article. The zinc coating on the balls prevents any contamination of the metal powder with iron and likewise prevents the wearing of the balls.

The ratio of the balls to metal is also of importance. The most rapid plating occurs when the ball-to-ball metal ratio is 2 to 1. By increasing this ratio, the metal coat can be made smoother and brighter. If the weight of the ball to metal increases, so does the finish of the plate. However, the weight of the metal plated on the article decreases. The range through which plating will occur is any ratio of balls to metal from 0 to 60 parts by weight of balls to 1 part by weight of metal powder or flake.

The fineness of the metal powder is also a factor in the plating operation and in the quality of the resultant coating. Small particles, for instance, .5 to 10 microns in largest dimension, are effective in producing heavy plating of desirable quality in economical times of treatment. The larger the plating particles the more they tend merely to receive and cushion the impact without developing enough intensity in surface to surface pressure to secure the particle permanently in place. The large impactor units, such as cracked shot, deliver energies in a certain range for a given treating apparatus and particles too large to be flattened and fixed in place by the impactor blows are ineffective and even interfere with the plating operation. For example, plus 100 mesh material screened out of a fine zinc dust hardly plates at all or gives only a light flash coat in a tumbling barrel about three feet in diameter and provided with riser bars lifting and dropping the material. Minus 200 mesh material of the same fine zinc dust (about .0025" and below) gives light coatings of approximately .0003" to .0004" in thickness, whereas the undersize, .5 to 20 microns in smallest dimension, segregated by screening through a fine cloth produces thick, well adhered coatings due no doubt to the greater efficiency of the impacting of the smaller particles and the decrease in the useless "cushioning" by the larger particles above 20 microns (in smallest dimension) which would have absorbed the blows more effectively applied on smaller particles. Such larger particles when present also parasitically accumulate these smaller particles in a manner still further increasing the bulk of the larger particles and aggravating their detrimental effects. As above noted, fine dust particles above 100 mesh were so large as to have practically no plating action and such light flash coat as appeared was largely due to the roughness or "tooth" of the plated surface.

Such "tooth" of the surface being plated is produced, for instance, by a brief acid strike and is helpful in gaining adherence of the plating particles. Even larger particles will wear off due to attrition on this roughness giving the characteristic thin film smoothing out the irregularities in a light flash coating which because of its smooth-

ness stops coating and will not accumulate any further deposit of these large particles. With the smaller particles, however, impacted in place, the "tooth" of the plated surface is particularly effective in intensifying the metal to metal pressures and securing adherence of the particles in place and subject to the further impacting as the treatment continues. This initial innermost layer of small particles at the plated surface is thus driven into intimate metal-to-metal contact with the said surface and bonded thereto by mechanical and atomic forces. Then the particles are impacted onto these innermost particles and bonded thereto in metal-to-metal contact in continuing deposits overlapping and interfitting in a most intimate surface-to-surface relation.

The crystalline growth of the particles into grains proceeds from particle to particle across the interfaces and constitutes a type of bonding recrystallization. This growth is largely in a direction flatwise or along the surface and at the innermost particles contributes to the bonding of the coating to the base metal with resultant relatively tenacious and durable adherence. The zinc coating still is in intimate metal-to-metal bond with the steel base even after the specimen was bent through four reversals. This coating was laid down at room temperature in a 16-hour run using mineral spirits and long-chain unsaturated fatty acid and substantially maintained its integrity throughout the bending with incipient cracking. Such cracking when further developed by bending will often break right through the individual crystals and with some fracture along a portion of the crystal boundaries. There is also a pronounced tendency of cracks eventually to form and follow along in the general direction of the surface while the innermost coating layer remains bonded to the base metal. These characteristics under stressed conditions again emphasize the layer-like formation of the coating with the flattened particles overlapping and interengaging like shingles; and it is this structure that develops the persistence with which the coating maintains its general form and adherence to the base metal under the bending stresses.

At ordinary temperatures there is no visible diffusion between the coating and the base metal, neither penetrating the other to any visibly evident extent. The metal-to-metal contact, however, is so intimate that a zinc coating laid down by this process will diffuse into the base metal (steel) at temperatures such as 225° C. well below the temperature at which such diffusion would be expected. This indicates that the bond is partly atomic and that there is atomic penetration between the metals long before a visible diffusion becomes apparent.

The bond between the coating and the base metal may thus be improved by heating within the melting point and this is increasingly true where between the base and the innermost layer of particles there are areas of an interface film intervening to reduce or prevent metal-to-metal contact. The longer or higher the heating the more evident the resulting diffusion. The large increase in surface area which takes place when the particle is flattened ruptures the thin film through the increase in surface area. Apparently this ruptured film is squeezed out by the forces involved between the clean surfaces which weld. Locally generated heat which is concentrated in the particle also might play a part in aiding the removal of the residual film. The very small size of the particle is of importance in the elimination of the major part of any film between the mating surfaces. Forces of capillarity may also function over the short distances involved. At the same time the bonding and recrystallization between the particles is accelerated. This final heating when employed may be to any desired degree preferably below the melting point of the softer metal and may advantageously involve an annealing of the base metal simultaneously improving its structure. It does not change and merely accentuates the characteristics of

the coating in providing an inexpensive and durable surface covering.

The temperatures of treatment particularly in the lower ranges may be attained by retaining the heat generated in the mass of material in the barrel. The recrystallization of the worked particles is initiated and continues during the treatment and subsequently and may be accelerated by subsequent heating after the articles are removed from the barrel.

In zinc coating it is desirable to use dust or powder which not only is fine but also of high porosity and little contaminated with oxide film. An effective zinc dust will approach zinc in color with only light filmings of oxide and will be uniform in composition. This responds readily to the coating procedure bringing the particles into intimate engagement with the base surface and with the layers as they are adhered, care being taken to provide the particle depositing treatment without excessive simultaneous particle removal. A satisfactory control of the coating deposit is attained in a rotary container on a horizontal axis and having a diameter of about eighteen inches with internal riser or stirring bars or lodges, the container rotating at about 40 r.p.m. A similar smaller cylinder of seven and one-half inches diameter is also effective rotating at about 60 r.p.m., the times of treatment varying from a few hours to sixteen or more hours as above explained and with various admixtures of coarser material such as cracked shot.

The following are examples of articles and coatings.

Example 1.—Two lbs. of roofing nails were degreased in a commercial alkali soak cleaner at 180° F. for five minutes. The nails were then rinsed in water and pickled in a 10% hydrochloric acid solution of 150° F. for five minutes. They were then rinsed in water. The nails were then placed in a one-gallon cylindrical can with six lbs. of zinc coated iron shot. The mixture was then covered with water. A few drops of an anti-foaming material were added together with 50 cc. of a solution containing 2 grams citric acid and 0.8 gram water soluble ethylene oxide condensed fatty acid type film-former such as is described in U.S. Patent Re. 23,861. 140 grams of zinc dust of 3 to 8 microns in particle size were added to the mixture before the can was closed. The can was then closed and placed in a paint shaking mechanism of a Red Devil paint shaker and shaken for 10 minutes. On opening the can, the zinc dust had been deposited on the nails as a dense, bright zinc coating of approximately .002" thick.

Example 2.—An assortment of small steel hardware two lbs. in weight were added to a small iron mill, approximately one-gallon capacity, containing "tin fats," "tin fats" being a hydrogenated mixture of fatty materials solid at room temperature used in the hot tinning of steel sheets. To the "tin fats" was added 50 cc. of oleic acid, 50 grams of copper powder and eight lbs. of iron shot which had been previously coated with copper in accordance with this example. The mill was closed and sealed with an asbestos gasket and operated in an insulated cabinet, maintained at a temperature of 200° C. When the mill was opened the hardware was found to be coated with a bright, attractive coating of copper approximately .001" thick.

Example 3.—A piece of steel degreased and acid pickled as described in Example 1, was taped round the edges to the bottom of a dish so it could not move and the dish was filled to a depth of 1 inch with a mixture of zinc dust, water and chemicals as described in Example 1. A brush having brass bristles was rotated over the surface of this steel plate rotating at a speed of 450 linear feet per minute. During rotation the dish was moved so as to place all portions of the steel surface under the action of the rotating brush. The plating operation was continued for two minutes, at the end of which time the steel was found to be coated with a bright, smooth, attractive coating of zinc.

Example 4.—A charge comprising 500 pounds of steel,

spring wire, hose clamps was descaled by blasting with steel grit and dipped for one minute in a solution of 2% CuSO_4 and 3% H_2SO_4 plus a commercial inhibitor at room temperature to deposit a thin coating of copper by chemical replacement. After rinsing, these were placed in a horizontal, octagonal tumbling barrel of 30" diameter and 30" length with 800 pounds steel pellets of .053" d. previously plated by similar operation of this process. To these were added 7½ pounds of zinc dust of 3-8 micron particle size, and ½ pound of tin powder of -325 mesh. Then 3 pounds of citric acid and 1 pound of a water soluble ethylene oxide condensed fatty acid type film-former such as is described in U.S. Patent Re. 23,861 were added together with sufficient water to cover the solid contents of the barrel. The barrel was then closed and rotated at a speed of 22 r.p.m. for one hour. The hose clamps were thus plated with a bright metallic coating of .0005" thickness containing zinc and tin.

As a result of tests that have been made and supervised by a United States Government testing agency for the Aeronautics Branch of the Department of the Navy in connection with the present invention, the following results were found to be factual and were so reported by that testing agency.

Electro-plate zinc coatings .0002" thick lasted between 190 and 273 days without rusting.

Electro-deposited cadmium coating .0002" thick lasted 364 days to first rust.

Electro-deposited cadmium coating .0005" thick no rust after 812 days.

Coatings of instant process .0002" thick no rust after 812 days.

It should be pointed out that cadmium has always been particularly good for exposure in marine atmosphere and in this particular test, as reported by the Government agency, the instant coating .0002" thick lasted as well as electro-deposited cadmium of 2½ times the thickness.

The above tests were made on coatings of steel bolts in out-door marine atmosphere.

The details of the polishing of surfaces of 125 and 560 and 500 diameters respectively are as follows:

- (1) Specimens polished completely dry from beginning to end.
- (2) Specimens polished very slowly on the following grits after having been rough polished to plane surface: Silicon carbide papers Nos. 1, 0, 00, 000, and 0000.
- (3) Specimens lapped on a "kitten's ear" cloth with "chrome buffing" compound as a polishing medium.
- (4) Final and very brief lap made with jeweler's rouge on "kitten's ear" cloth.
- (5) Specimens washed with alcohol.

The polishing and etching of the reproduction 1000 diameters is as follows:

- (1) Mount specimen in circular steel ring in Bakelite matrix.
- (2) Rouge polish with coarse abrasive or file making sure steel is removed to a point where a full coat is exposed.
- (3) Wet polish in the following order on Carborundum papers, grit 240, grit 320, and grit 400.
- (4) Polish on lead lap with 303½ emory.
- (5) Polish on wax lap with 600X crystalline Alundum.
- (6) Polish on AB microcloth lap with Linde B polishing compound, after having treated the lap with a light solution of castile soap.
- (7) Maximum amount of pressure should be used on the final wheel, solution kept as thick as possible and polishing time kept to a minimum.
- (8) Etch with a chromic anhydride reagent, such as the following: 50 grams of pure CrO_3 ; 4 grams Na_2SO_4 ; 1000 mls. of H_2O .
- (9) Etching time normally should not exceed 2 seconds, flushing off excess reagent with water, following by swab with alcohol.

Another specimen at 500 diameters and etched as above described has the grain characteristics at adjacent areas of variable working. The particles are similar in general form to those previously described, and intensified attrition and impacting of the coating particles as they round a corner bend stretches and thins out the graining to films along closely packed lines following the contour of the base surface.

The coatings are thoroughly protective. They are at least equal to hot dip and electro deposited coatings in durability and service. In uniformity of thickness, adherence, flexibility and continuity they are similarly comparable to the hot dipped and electroplated coatings of the same metal.

While the treatments above described have dealt mainly with the deposit of particles of a single metal such as zinc, the process of this invention is also applicable with a plurality of powders of different metals or of particles of alloys both solid solution and two-phase, as explained in my applications, Serial Nos. 14,639 and 77,269, and the metal coatings referred to in the appended claims are of one or more metals or alloys.

I claim:

1. An article having a pressure applied metallic coating of built-up layers of numerous mechanically flattened overlapping and interfitting discrete and distinct particles of metal, said particles having clean substantially pure metal surfaces and being atomically bonded together by intimate metal to metal contact at portions of said clean surfaces; and a film-forming, surface-active organic substance interspersed throughout the coating in the form of inclusions of thin, strongly adherent film on and between the unbonded clean surfaces of the particles to prevent exposure and inhibit oxidation of the unbonded clean surfaces of the particles, each inclusion aiding in holding together the particles adjacent the inclusion through the said unbonded surfaces of the particles to which the organic substance adheres, said organic substance being substantially chemically inert to the clean metal and having a polar molecular structure including a carbon chain and capable of exhausting itself through adsorption of molecularly thin films onto the clean surfaces of the metal, and the thin film being physically affinitive and strongly adherent to clean surfaces of the metal.

2. An article according to claim 1 and further having distributed inclusions of a water soluble fluxing compound chemically reactive to oxides of the metal when in aqueous solution, the film-forming organic substance having selectively greater adherence to the clean metal surfaces such that the inclusions of the fluxing compound are spaced from the clean metal surfaces by the molecularly thin film of the film-forming substance.

3. An article according to claim 1 wherein all of the particles before mechanical flattening are between .5 and 20 microns in their largest dimension.

4. An article having a pressure applied metallic coating of built-up layers of numerous mechanically flattened overlapping and interfitting discrete and distinct particles of metal, said particles having clean substantially pure metal surfaces and being atomically bonded together by intimate metal to metal contact at portions of said clean surface; a film-forming, surface-active organic substance interspersed throughout the coating in the form of inclusions of thin, strongly adherent film on and between the unbonded clean surfaces of the particles to prevent exposure and inhibit oxidation of the unbonded clean surfaces of the particles and to aid in holding together the particles through the said unbonded surfaces to which the organic substance adheres, said organic substance being substantially chemically inert to the clean metal and having a molecular structure including a carbon chain and capable of exhausting itself through adsorption of molecularly thin films onto the clean surfaces of the metal, and the thin film being physically affinitive and strongly adherent to clean surfaces of the metal; and a water solu-

ble fluxing compound chemically reactive to oxides of the metal when in aqueous solution distributed in inclusions in the coating to a lesser extent than said film-forming substance.

5. An article according to claim 4 wherein all of the particles before mechanical flattening are between .5 and 20 microns in their largest dimension.

6. An article having a pressure applied metallic coating of built-up layers of numerous mechanically flattened overlapping and interfitting discrete and distinct particles of metal, said particles having clean substantially pure metal surfaces and being atomically bonded together by intimate metal to metal contact at portions of said clean surfaces; and a film-forming, surface-active organic substance interspersed throughout the coating in the form of inclusions of thin, strongly adherent film on and between the unbonded clean surfaces of the particles to prevent exposure and inhibit oxidation of the unbonded clean surfaces of the particles, each inclusion aiding in holding together the particles adjacent the inclusion through the said unbonded surfaces of the particles to which the organic substance adheres, said organic substance being substantially chemically inert to the clean metal and having a polar molecular structure including a carbon chain and capable of exhausting itself through adsorption of molecularly thin films onto the clean surfaces of the metal, and the thin film being physically affinitive and strongly adherent to clean surfaces of the metal, the thin film of organic substance further being adherent to the clean metal to a degree greater than to oxides of the metal.

7. An article having a pressure applied metallic coating of built-up layers of numerous mechanically flattened overlapping and interfitting discrete and distinct particles of metal, said particles having clean substantially pure metal surfaces and being atomically bonded together by intimate metal to metal contact at portions of said clean surfaces; a film-forming, surface-active organic substance interspersed throughout the coating in the form of inclusions of thin, strongly adherent film on and between the unbonded clean surfaces of the particles to prevent exposure and inhibit oxidation of the unbonded clean surfaces of the particles and to aid in holding together the particles through the said unbonded surfaces to which the organic substance adheres, said organic substance being substantially chemically inert to the clean metal and having a molecular structure including a carbon chain and capable of exhausting itself through adsorption of molec-

ularly thin films onto the clean surfaces of the metal, and the thin film being physically affinitive and strongly adherent to clean surfaces of the metal; and a water soluble fluxing compound chemically reactive to oxides of the metal when in aqueous solution distributed in inclusions in the coating to a lesser extent than said film-forming substance, the thin film of organic substance further being adherent to the clean metal to a degree greater than to oxides of the metal.

8. An article having a pressure applied metallic coating of built-up layers of numerous mechanically flattened overlapping and interfitting discrete and distinct particles of metal, the particles before mechanical flattening being .5-20 microns in their largest dimension, said particles having clean substantially pure metal surfaces and being atomically bonded together by intimate metal to metal contact at portions of said clean surfaces; and a film-forming, surface-active organic substance interspersed throughout the coating in the form of inclusions of thin, strongly adherent film on and between the unbonded clean surfaces of the particles to prevent exposure and inhibit oxidation of the unbonded clean surfaces of the particles and to aid in holding together the particles through the said unbonded surfaces to which the organic substance adheres, said organic substance being substantially chemically inert to the clean metal and having a molecular structure including a carbon chain and capable of exhausting itself through adsorption of molecularly thin films onto the clean surfaces of the metal, and the thin film being physically affinitive and strongly adherent to clean surfaces of the metal, the thin film of organic substance further being adherent to the metal to a greater degree than to oxides of the metal.

9. An article according to claim 8 wherein the organic substance is a cationic, emulsifying agent capable of rendering the metal surfaces water rejecting.

10. An article according to claim 8 wherein the organic substance comprises a cationic wetting agent, and includes a water soluble oil mixed therewith.

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