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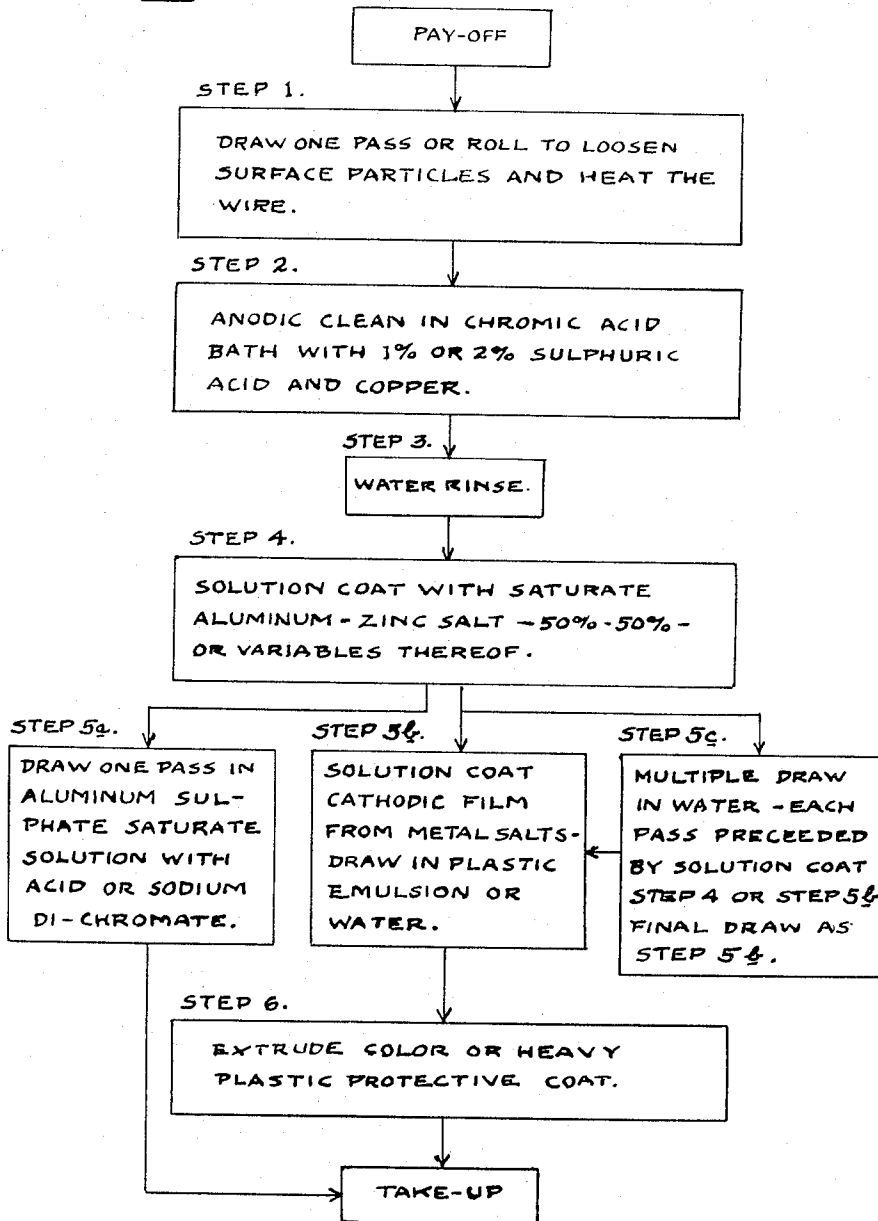
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PROCESSES FOR DRAWING AND COATING METAL SUBSTRATES

Filed March 3, 1967

2 Sheets-Sheet 1

Fig. 1.



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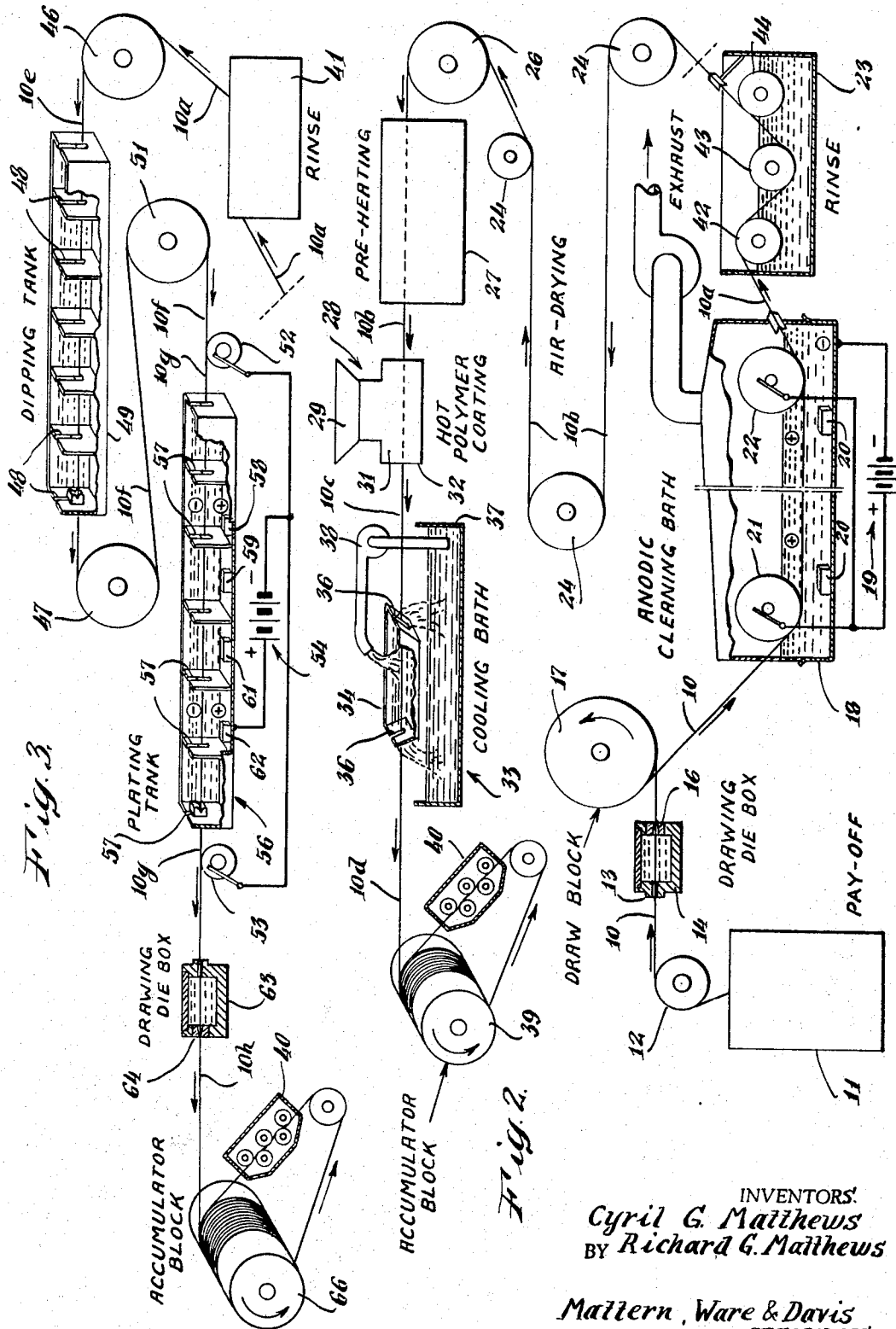
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**PROCESSES FOR DRAWING AND COATING METAL SUBSTRATES**

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Continuation-in-part of application Ser. No. 359,763, Mar. 10, 1964. This application Mar. 3, 1967, Ser. No. 620,547

10 Claims. (Cl. 204—32)

**ABSTRACT OF THE DISCLOSURE**

Processes for applying firmly bonded coatings of metals or polymers to metal wire substrates by passing the longitudinally-moving substrate through a cold drawing die and then through an anodic cleaning bath in a cleaning solution of chromic acid containing free metallic copper, followed by either preheating, hot polymer coating and cooling steps, or by subsequent metallic coating steps including an electroplating bath of metallic salts either preceded or replaced by a dipping bath of metallic salts and followed by passage through a second drawing die, with all operations being performed simultaneously as the wire substrate passes successively at standard high coating speeds of several hundreds of feet per minute from a storage source through the foregoing operations to a rotating accumulator block drum, or suitable take-up means.

**CROSS REFERENCE TO RELATED APPLICATION**

This application is a continuation-in-part of our co-pending joint application Ser. No. 359,763, filed Mar. 10, 1964.

**BACKGROUND OF THE INVENTION**

Conventional processes for coating metal substrates with polymer coatings have encountered numerous adhesion or bonding problems. In fabricating colored wire hooks and eyes for garments and undergarments such as dresses, brassieres and corsets, for example, steel wire may be coated with nylon or other polymers incorporating pigments selected to match the garment fabric color, giving a highly attractive, non-metallic appearance. Bonding of the polymer coatings to the steel wire has proved so difficult in the past that coatings 0.005" thick have been considered necessary to withstand conventional "salt spray" tests, and to provide a polymer layer thick enough to block atmospheric air and moisture in order to avoid corrosion of the wire surface under the polymer.

In the art of plastic coated wire, corrosion of the metal surface under the plastic coating has been a particularly difficult problem due to the fact that plastic materials, especially thermoplastic resins, are sufficiently porous that in thin film of the order of .001" or .002", for example, moisture and gases can permeate through to the base metal causing oxidation, with a resulting loss of plastic adhesion and consequent coating failure. The presence of loose oxides in the usual metal coatings, such as galvanized, tinned or coppered coatings, prevents the firm anchorage necessary to permit forming or drawing of the material after the plastic has been applied, so that plastic coated wire has not been satisfactory for uses involving subsequent forming or drawing. Indeed, drawing of such conventional polymer-coated wire often tears or shears off the polymer coating in the drawing dies, rendering it impossible to compact or densify such polymer coatings enough to make them impermeable to atmospheric gases or moisture.

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With prior wire-coating techniques, adequate metallic coatings could not be bonded to the moving wire at economically-practical high coating speeds; instead, slow and lengthy coating operations were required.

**SUMMARY**

The processes of the present invention all take advantage of the discovery that passage of the metallic substrate through an anodic cleaning bath incorporating a chromic acid solution containing free metallic copper cleans the substrate by removing accumulated oil, wax, lubricants and oxides with high effectiveness, leaving a bare metal surface exposed for subsequent coating operations, and also leaves on the metal surface a residual film containing both chromium and copper, which provides unexpectedly strongly adherent bonding of subsequent metallic or polymer coatings to the underlying substrate.

The residual copper-chromium film is extremely thin, but its presence has been verified by spectrographic analysis performed by emission spectrography, establishing that steel wire passed through the anodic cleaning baths of this invention incorporates from 0.01 to 0.05% chromium, and from 0.01 to 0.10% copper. Since anodic cleaning would normally be expected to remove positive ions from the advancing wire, it is believed that this residual copper-chromium film may be deposited after the wire leaves the exit sheave which guides it beneath the bath surface and supplies the wire's positive "anodic" potential; after leaving this exit sheave, the wire has no electrical potential, and it remains immersed in the cleaning bath containing free copper and free chromium ions for an appreciable length of time, during which the chromium-copper film observed by emission spectrography is apparently formed on the surface of the metal substrate.

This anodic cleaning bath of chromium-copper solution is highly useful in processes for coating previously galvanized wire, for the zinc coating appears to accept the chromium-copper film with a firmly adhering bond, providing an unusually strong bond with later-applied coatings of polymer or of metallic aluminum, zinc or copper.

Polymer coatings only one or two-thousandths of an inch in thickness, when applied by the processes of this invention, provide exceptionally good protection and far longer useful life than conventional coatings.

Accordingly, a principal object of the invention is to provide processes for coating metal wire and other metal substrates at high speeds with highly adherent coatings of polymers, aluminum, zinc, copper or other metals.

Another object of the invention is to provide such processes incorporating an anodic cleaning operation performed in a cleaning solution containing both chromic acid and free metallic copper, in which the metallic substrate to be coated remains immersed for an appreciable length of time after the anodic potential is removed therefrom.

A further object of the invention is to provide such coating processes in which the anodic cleaning bath is formed of a solution of chromic acid containing a small amount of sulfuric acid, with one or more blocks of solid, metallic copper being immersed in the bath.

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.

FIGURE 1 is a schematic flow diagram of several alternative embodiments of the processes of this invention;

FIGURE 2 is a schematic diagram of the equipment and process operations employed in preferred processes of the invention for coating metal wire with polymer coatings; and

FIGURE 3 is a similar, fragmentary schematic diagram of the terminal equipment and process operations employed in other alternative processes for applying metallic coatings to metal wire which has already passed through a portion of the process operations shown in the diagrams of FIGURES 1 and 2.

#### PREFERRED EMBODIMENTS

In the diagram of FIGURE 1, a series of successive steps employed in several alternative processes of the invention are illustrated, and these steps will be described in detail below. In the production line illustrated schematically in FIGURE 2, these successive steps are shown as successive process operations.

At the lower left corner of FIGURE 2, a wire 10 is shown advancing from a pay-off storage source, a core, reel, or storage drum 11, passing over one or more guide sheaves 12. The advancing wire then passes through a wiping entrance gasket or "wipe-back" 13 of plastic foam, sponge rubber or any similar deformable gasket material which substantially closes an entrance aperture communicating with the hollow interior of a die-box 14, forming a reservoir of water or other liquid lubricant for the cold drawing operation to follow.

Opposite the entrance aperture of die-box 14, an exit aperture therefrom has anchored therein a finely-machined die block 16 having as a central aperture passing therethrough an internally-converging cold drawing die aperture. The wipe-back 13 and the surface tension meniscus formed in the fine die aperture in die block 16 both prevent the leakage of lubricant liquid from die-box 14 through its entrance or exit apertures, and the leading end of a fresh length of wire is filed down to a reduced diameter taper for initial threading through die block 16.

Hereinafter, the terms "drawing through," "drawing from" or "drawing in" coating solutions, water, polymer or monomer suspensions or liquid lubricants should be deemed to mean the drawing of wire through a drawing die block forming the exit aperture of a die-box such as die-box 14 containing the specified liquid material, through which the wire travels as it approaches the die block.

As shown in FIGURE 2, drawing tension required to draw the wire through the drawing die, reducing its diameter by several thousandths of an inch or from about 5% to about 15% or more of its entering diameter, is provided by frictional engagement of the wire led from the cold drawing die as it passes in one or more turns around the periphery of a "draw block" 17, which may be a power-driven sheave or cylindrical guide, preferably formed as a large, heavy rotating mass affording the stabilizing effect of a flywheel to govern the tension and the velocity of advance of the wire through the successive stages of the processes of the invention.

From the draw block 17, the advancing wire 10 passes through a suitable entrance aperture into a stainless steel tank 18 containing an "anodic" cleaning bath, so-called because the wire 10 becomes the anode or positive terminal in an electrolytic cell therein, with the metal tank 18 itself being the cathode or negative terminal. The D.C. potential between wire 10 and tank 18 is maintained at about 6 volts by a voltage source 19, such as a heavy-duty commercial rectifier, preferably rectifying single-phase 110 volt A.C. line voltage at a rated current ranging between 50 to 100 amperes. As indicated in FIGURE 2, the voltage source 19 supplies its positive "anode" potential to the wire 10 through brushes and slip rings connecting in parallel two wire-guiding sheaves, an entrance sheave 21 and an exit sheave 22, which are insulated and rotatably mounted in the walls of the tank 18 to guide the wire 10 submerged beneath the surface of the anodic cleaning bath along the greater part of the length of the tank 18.

The electrolyte solution in tank 18 which produces highly successful results is a mixture of chromic acid

with a small amount of sulfuric acid, and one or more solid metallic copper blocks 20 are immersed therein to provide free copper ions. The preferred constituents of the anodic cleaning bath in tank 18 and the phenomenon believed to be responsible for the resulting thin copper-chromium film on wire 10 after it leaves tank 18 are described in more detail hereinafter.

From tank 18 the wire 10, here identified as 10a in FIGURE 2, passes through one or more fresh water rinse baths 23, preferably of circulating or flowing tap water, to rinse off all excess unbonded solution from the anodic cleaning bath. The wire then travels as wire 10b through an air-drying stage, guided by drying sheaves 24, bringing the advancing wire to a final guide sheave 26 which aligns it for passage through a preheating stage at a preheating station 27, from which it passes directly into a hot polymer coating unit 28. In unit 28, pellets of nylon are loaded into a hopper 29, from which they pass downward through a heating zone 31 to a heated molten polymer coating chamber 32.

The chromium-copper film received by the wire 10a during its passage through the anodic cleaning bath in tank 18, coupled with the preheating of the wire in unit 27 and the heating of the polymer in zone 31 and chamber 32, apparently all cooperate to provide an unexpectedly tough and adherent bond between the polymer coating and the underlying substrate wire.

The polymer-coated wire 10c leaving the coating chamber 32 of coating unit 28 carries a hot, soft polymer coating, which is cured by rapid air cooling, and also by a recirculating bath 33 of cooling water through which the wire passes. Preferably, as shown in FIGURE 2, the cooling bath 33 takes the form of an elongated tank 34 having ends with deep vertical notches 36 formed therein, aligned for wire 10c to pass through tank 34 between notches 36. Cooling water is drawn from an underlying sump tank 37 by a pump 38 which delivers it to tank 34. Water in tank 34 overflows continuously through notches 36 into sump tank 37, and is continuously re-cycled by pump 38.

The cooled wire 10d advancing from cooling bath 34 is led directly to make one or more turns around an "accumulator block" 39, preferably formed like draw block 17 as a large, heavy, power-driven, rotating sheave or drum having considerable flywheel inertia, and co-acting with draw block 17 to maintain the desired tension in wire 10 as it passes through its successive stages of the coating process as wire 10a, 10b, 10c and 10d.

Blocks 17 and 39 can be advantageously linked together mechanically for synchronized rotation, giving excellent control of the speed of advance and the tension in wire 10 as it proceeds through the coating operations shown in FIGURE 2. The accumulator block 39 is preferably drum-shaped to provide collection and temporary storage of the arriving coated wire 10d, from which the wire can periodically be tied off, segregated and packed for permanent storage or shipment. The arriving wire passing around accumulator block 39 may be led around a companion sheave and through a conventional wire straightener 40 if desired, before it is collected for storage on block 39, as shown in FIGURE 2.

#### METAL COATED WIRE

The terminal series of coating stages shown in FIGURE 3 follows the preliminary stages performed in units 11 through 22 shown in FIGURE 2, and the wire 10a leaving the anodic cleaning bath in tank 18 corresponds to the wire 10a entering the rinse bath 41 shown at the lower right corner of FIGURE 3. As will be fully explained in actual examples below, rinse 41 may be either a water rinse or a preliminary rinse in a bath of metallic salts. Structurally, it preferably corresponds to rinse bath 23 shown in FIGURE 2, where the arriving wire passes over an entrance guide sheave 42, beneath a submerging sheave 43 carrying it beneath the surface of

the rinse path, and thence over an exit guide sheave 44, from which it passes to the subsequent stages of the coating process.

In the metal-coating processes shown in FIGURE 3, these subsequent stages involve the immersion of the advancing wire in one or more various dipping or plating tanks or lubricant dips, and therefore the drying operation employing air-drying sheave 24 and the pre-heating unit 27 are not required. Instead, after passing through rinse bath 41, the wire 10a passes around a first guide sheave 46 which aligns it with a second guide sheave 47. The span of wire 10e stretching between sheaves 46 and 47 preferably forms a substantially straight line, and is thus self-aligned for passage through a series of successive aligned, deep, vertical notch apertures 48 formed in successive partitions separating the various compartments of a multi-compartment dipping tank 49, containing dip solutions of metallic salts described more fully below. At each notch 48, if desired, a wipe-back of plastic foam or sponge rubber similar to gasket 13 may be used to assure wiped contact of the dip solution with the advancing wire immersed therein, and to minimize mixing of successive dip solutions when different compartments of tank 49 contain different dip solutions.

After leaving dipping tank 49 and passing around the second guide sheave 47, the dip-coated wire 10f passes over a third guide sheave 51, after which it is aligned by passing around a first cathodic contact sheave 52 and thence in a substantially straight, taut span through the length of a plating tank 56, to and around a second cathodic contact sheave 53. Sheaves 52 and 53 connect the wire 10f to a heavy-duty source 54 of up to 6-volt D.C. electroplating potential, with the negative or cathode terminal of the source 54 now being connected to wire 10f via suitable brushes and slip rings mounted on the insulated shafts of sheaves 52 and 53, which are thus connected in parallel to supply negative plating potential to the wire. The positive or anode terminal of source 54 is directly connected to the plating tank 56, which is preferably provided with separate solution compartments separated by partitions having aligned deep vertical notches 57 formed therein, similar to aligned notches 48 formed in the partitions of dipping tank 49. After passing around sheave 52, wire 10f may now be designated 10g, as shown in FIGURE 3, to indicate the station where it passes successively through notches 57 for exposure to electrolytic plating solutions and potential in successive compartments of plating tank 56. Examples of successful electrolytes and additive blocks of anode metals 58, 59, 61 and 62 placed in different compartments of plating tank 56 will be described in detail below.

As with dipping tank 49, wipe-back gaskets of sponge rubber may be mounted in the successive partition notches 57 of tank 56 to minimize mixing of separate electrolytes in different compartments of tank 56.

Either or both of tanks 49 and 56 may be used, as will be described in more detail below.

After leaving the plating tank 56, the plated wire 10g passes around second cathode contact sheave 53, as described above, and thence preferably through a second drawing die-box 63, containing a reservoir of lubricant or a polymer or monomer emulsion to be described more fully below, and provided in its exit aperture with a reducing, drawing die block 64 similar in all respects to die block 16 in FIGURE 2. Drawing through die block 64 assures uniform finished diameter of wire 10g, polishes its finish, and leaves thereon a final thin film of lubricant to give glossy appearance and protection against atmospheric corrosion. From die block 16, the finished wire 10h is coiled on an accumulator block 66 similar to block 39, and provided with a companion wire straightener 40 if desired.

#### CLEANING, DIPPING AND PLATING LIQUIDS

The coating processes of the invention are here de-

scribed in terms of their use as a continuous in-line wire coating procedure including the drawing of the metal wire, although it will be understood that the invention also contemplates the coating of strip or sheet metal in which case suitable rolling means will be employed in place of the drawing dies employed in the drawing of wire. It also applies to ferrous as well as non-ferrous materials.

As shown in the charts of FIGURES 1 and 2, a steel wire, either bare or galvanized, is fed from a pay-off stand 11 through Step 1 of the process which consists in drawing the wire through a suitable cold drawing die 16 for one draft in the usual soap, oil or other suitable drawing lubricant, or pulling through turks head rolls with no lubricant, or through breaker rolls to loosen scale or oxides. The purpose of this initial cold drawing or rolling is to loosen any oxides or other deposits and to heat the wire. It has been found that the heat so generated aids in the cleaning and coating of Step 2. This initial drawing also reduces the wire diameter, and "sets" the zinc coating on galvanized wire, making it more dense and uniform.

Step 2 consists in quenching the wire in an anodic cleaning bath in tank 18 containing a solution of chromic acid in suitable amount, and about 1%-2% free sulphuric acid, in which copper in the form of solid metal (not a salt) is introduced, with the copper 20 preferably being placed on the floor of the tank. It has been found that the amount of copper released into solution from the immersed copper blocks 20 is determined by the concentration of acid present. Hence any refreshing of the bath with additional chromic acid should be accompanied by the addition of 1% or 2% of sulphuric acid.

The normal characteristic of a copper-free chromium solution is that the chromium does not react with the iron exposed by cleaning. The presence of this small amount of metallic copper, however, apparently acts as a cross-linking agent or catalyst, with the result that the copper-activated chromium reacts with the exposed iron, and leaves an unbroken film of chromium compound or alloy on the surface of the steel wire base.

While a deposit of chromium copper alloy may be obtained by simple immersion of cleaned wire the process is hastened by running the amperage higher than normally recommended for anodic cleaning of a given size and grade of material, apparently resulting in formation of the desired chromium-copper alloy or compound in a thin coating or deposit, during the time the cleaned wire is immersed in the cleaning solution while it passes from the energized second guide sheave 22 toward the exit of cleaning bath 18, as shown in FIGURE 2.

This film deposit is so adherent that it not only will not wipe or rinse off, but is ductile to the extent that it can be immediately drawn, rolled, or otherwise deformed without exposing the base metal. Most important, it apparently will instantly react with most metals in solution to form alloys of those metals. These metals can be selected for particular properties and functions. For example, tin, lead, or similar bearing metals may be deposited to permit drawing or rolling. Alloys of nickel, manganese, aluminum and other surface hardening alloys can be provided for hardness or resistance to abrasion or heat. Both electrically conductive and non-conductive coatings thus become possible. If a plastic coating is desired, it can be extruded on the wire at the finishing speed, as shown in unit 28 in FIGURE 2, with excellent bonding adherence.

Hence, the film coating is in effect a conversion coating made possible by the discovery that small percentages of copper dissolved in a standard chromic acid solution will act as a catalyst for depositing a thin coating of chromium-copper alloys or compounds on iron or steel in a manner similar to that experienced in a cop-

per salt bath alone. This does not occur when copper is not present in the cleaning solution.

Returning to FIGURE 1, Step 3 consists in a water rinse of the wire as it emerges from the cleaning tank 18. It is important this rinse be thorough, as traces of the liquid solution of chromic acid and sulfuric acid are highly destructive to the coating and to the base metal.

In the processes shown schematically in FIGURES 1 and 3, Step 4 consists of passing the wire through a dipping tank 49 containing a solution, preferably saturated, of a suitable metal salt to react with the chromium compound or alloy film. Rubber wipes, preferably formed of pads of foam rubber clamped to wipe the advancing wire in notches 48, are used to bring the solution into intimate contact with the metal surface and secure a deposit of metal from the dipping solution thereon. The metal salt solution so used would depend on the base film and on the desirability of the metal in the subsequent operations and end use. For both the decorative and protective coating of steel, an alloying film of aluminum and zinc has been found highly desirable for most applications involving subsequent drawing or forming. Aluminum in itself reacts too slowly and zinc in itself is too brittle. The combination of the two results in a fast reactive deposit with excellent ductility. The alloy film seems to have excellent properties at about a 50%-50% ratio solution of the salts of the two metals. By breaking the tank 49 down into separate compartments containing different solutions, as shown in FIGURE 3, this film can be applied initially at a high zinc, low aluminum content, and can finish with virtually pure aluminum in the outer surface of the film if desired. Further, where only one subsequent pass in rolling or cold drawing at die block 64 is to be employed, an extremely hard and yet flexible film can be developed from this bath by placing any of the acids used as electrolytes for the anodizing of aluminum therein.

Plating in electroplating tank 56 may follow dipping in tank 49, as described more fully in the examples below.

Step 5a: Where only one sizing drawing pass is made in die block 64, and an aluminum finish is acceptable for the end use, the acid bath mentioned in Step 4 may be employed as a "lubricant" in the drawing operation, with the wire passing therethrough in die-box 63. This is not recommended where a subsequent plastic coating is to be applied, as the salt carry-over will not give a firm base for the plastic and will prevent any chance of cross-linking such a coating with the base metal. The acid we have found best and recommend in such case is a solution of sodium di-chromate at about 1% by weight.

Step 5b: Where only one drawing pass is desired in die block 64, and a finish is to be obtained for protection and decorative purposes and for bonding a subsequent plastic coating, a film of aluminum-zinc alloy is employed and the drawing employs as a lubricant a water bath preceded by a water rinse (not shown) to remove the loose salts carried over from Step 4. Preferable to this, however, is the application of a second bath immediately following the aluminum-zinc treatment in tank 49. The aluminum-zinc treatment in tank 49. The aluminum-zinc film being "anodic" to the base metal in the Galvanic Series table of metals and alloys interacting to produce corrosion by electrolysis, therefore corrosion resistance is improved by applying a "cathodic" film in a second dipping tank (not shown), and of the many which are highly reactive, one which is highly decorative and protective has been found in a combination of tin and nickel. In this we employ a recommended amount of approximately 65% tin to 35% nickel based on metal content of the salts used. Cold drawing following this bath may follow a water rinse (not shown), or with water in the die-box 63, or through a dilute rinse of stannous chloride or stannous sulphate, with a water emulsion of a suitable plastic in the die-box 63. The carry-over after wiping of the metal salt used in

the rinse will apparently serve to catalyze the plastic emulsion and aid in its bonding to the metal film, and plastic monomers such as caprolactam are apparently polymerized to some extent, perhaps by the heat and pressure induced by cold drawing in die block 64. The addition of small amounts of copper to the tin-nickel bath will give a simulated gold color, as little as 2% being effective.

Step 5c: In the case of more than one cold drawing pass being desired, either or both of two methods can be employed, one by using a multiple number of passes through the bath or Step 5a, and finishing with the bath of Step 5b, or the reverse. All intermediate passes should of course be drawn in water and no free acid employed.

Step 6: A highly satisfactory product may be obtained for many applications with the product emanating from Step 5b and/or Step 5c. However, where color characteristics are desired a heavier film of plastic will have to be applied. Heavier coatings of plastic may also be desired to give added protection. In such cases an "in-line" flow-coating or extruding operation can be employed, as shown in FIGURE 2. In this case, final cold drawing may be omitted, as in FIGURE 2. The type of emulsion in the final die-box, if any, should be such that its film will chemically combine with the type of plastic being used in the top film. If such is not available, then the last cold drawing pass should be made in water and a suitable metal stabilizer, catalyst, pigment or the like introduced into the top coating to obtain chemical cross-linking with the metal film last applied.

It is pointed out that the arrangement of tanks, draw dies, rubber wipes, plastic extruder, pay-off stand and take-up machine shown schematically in FIGURES 2 and 3 follow known practices in the drawing and coating of wire. In the case of strip or sheet, suitable rolls are employed in the place of the cold drawing dies 16 and 64 according to known procedures.

All coatings produced by this method should be allowed to age harden 24-48 hours before subjecting them to any severe forming operations or outdoor weathering.

The following is a summary of advantages of our procedure.

Prior to the application of any coating, cleanliness is necessary. Drawing compounds as normally applied, namely wax, soaps and greases, must be removed. This can be a slow operation compared to cold drawing. As cleaning in our method is done at the starting size and the surfaces kept clean through multiple drawing, it is evident the finishing speed is greater than if the wire had to be cleaned at the final size.

In present commercial applications the coating of wire and strip is done as a separate operation from cold drawing. In our method it is done in the same operation.

By proper cleaning, tank design and control, we have found it possible to clean and coat in the same tank 18 with our method, and other advantages include the ability to produce non-porous coatings in thinner films than could otherwise be applied, and the production of coatings at wire-drawing speeds rather than at the commercial speeds of tinning, galvanizing, etc.

In addition to the operational cost advantages cited above it is obvious that, material-wise, low-cost water soluble metal salts will be employed instead of rare metals employed as expensively controlled molten baths or high cost anodes by other coating processes.

The elimination of free acids in the system such as normally used in plating, except when plating tank 56 is employed, not only eliminate the acid expense but contribute to minimize rinsing as well. Also, the danger of acid embrittlement of either the coating or base metal is thus avoided.

In practice, it has been observed that, subject to good cleaning practice, increased speeds result in improved pick-up of metal and improved coatings. This we believe is due not only to additional pressure and additional frictional heat created by the speed increase but by static elec-

tricity built up by the wire passing through the tight rubber wipes as well.

Another observation is that the coatings as well as the ability to draw in water have the effect of adding heat "insulators" in the drawing dies, so that the latter remain at substantially room temperature. The films produced by the processes of this invention are so strong that even though a die is scratched by a fin or other imperfection in the base metal there is generally no fracture in the protective metal coating being applied. Hence, improved physical results are obtainable through less strain to the surface of the base metal in our method of cold drawing. This is highly desirable in processing such wires as rope, tire bead, valve-spring, music wire, etc.

Alloys of metal from salts in solution may be deposited, which alloys might not be obtainable in an electroplating or molten bath method.

All commercial finishes applied to steel today are either galvanically anodic or cathodic to the base metal in the Galvanic Series, and are hence limited in application and useful life. Our coatings being both anodic and cathodic are superior for many given applications. This it is expected will eliminate the need for plating parts after forming, as is conventionally done for protective purposes on many wire and strip applications.

Extremely thin and yet non-porous films of precious metals can be obtained at speeds of cold drawing and of quality far in excess of that produced by normal electroplating procedures. These metal salt baths can further be harmless sulphates, nitrates or chlorides, rather than the toxic cyanide baths normally in use.

Following this same procedure brass wire as used for safety pins, hooks and eyes, etc. can be cold drawn to give a simulated nickel plate appearance and eliminate the present expense of plating after forming, as is now done.

In the case of heavy plastic films, that is, greater than 0.0005", it has been found that they will, within the elongation limits of the coating as applied, lend themselves to further drawing. This drawing after coating increases the tensile strength, hardness and density of these films, just as in molecular-oriented "monofilament" plastic strands. For example, nylon so processed has been made so non-porous that it would not accept a color dye.

It has also been found that metallic particles such as aluminum powder "pigment" distributed throughout the external plastic coating apparently produce a chemical or molecular bond at the interface with the underlying chromium-copper film, further enhancing the toughly-adhering bond between plastic coating and metal wire substrate.

Those film-coated substrates with a heavy plastic outer coating can be heat sealed to themselves or porous fabrics such as cotton, linen and other plastics, etc. Such heat sealing can eliminate expensive sewing operations without losing their adhesion to the base metal.

In this process high carbon wire or strip may be tempered to a degree comparable to that of commercial oil tempered material. Cold working after tempering by drawing or rolling will raise the tensile and yield point, to further improve the tempering which has taken place in the cleaning bath. In this processing of high carbon wire it is important that the sulphuric acid level be held to 1% or less, to avoid embrittling the steel. This eliminates the expensive extra operation now employed where high heats for quenching and "drawing" the temper are necessary. It will also eliminate the need of normalizing or stress relieving springs after forming and hence avoid not only the expense of this operation but avoid damage to plastic coatings already applied to such springs as well.

COATING OF GALVANIZED WIRE

When the hot galvanized steel wire is subjected to the nylon coating process illustrated in FIGURE 2, the chromium-copper film applied to the wire in the anodic clean-

ing tank 18 apparently permits the overlying nylon layer to achieve an unusually tough and adherent bond to the underlying, film-covered metal substrate. The bond between metal and plastic is so unusually strong that plastic actually remains adhering to the sheared ends of the coated wire after it has been formed into hooks and eyes severed from each other, ready to be sewed onto binding tapes for stitching into garments. Nylon-coated, galvanized steel wire eyes formed from coated wire produced by the techniques of the present invention and sewed to sample binding tape have been subjected to the salt spray exposure test prescribed by Federal Specification 141, Method 811, employing a 20% salt spray for a period of 96 hours. These white-nylon coated wire eyes remained bright white in color, exhibiting no trace of corrosion, rusting or discoloration whatever. Even the sheared ends of the wire formed into these eyes show no trace of corrosion, and sharp bends in the formed eyes where the nylon coating was stretched thinly to reveal the underlying wire show no trace of rust or corrosion. In this test, a comparison tape carrying conventional wire hooks was subjected to the same 96-hour salt spray test, and every hook is badly rusted, discoloring the fabric severely.

ANODIC CLEANING BATH SOLUTION

In the various processes described herein and illustrated schematically in the drawings, the anodic cleaning bath of Step 2 in tank 18 preferably employs an aqueous solution of the following parts by weight:

	Percent
0.27 part concentrated sulfuric acid, 66° Baumé -----	0.16
26.90 parts BFC "flake chromic acid," CrO <sub>3</sub> of 99.75% purity, sold by Essex Chemical Corporation -----	16.34
137.50 parts water -----	83.50
Total -----	100.00

In the apparatus shown schematically in FIGURE 2, the tank 18 is approximately 10 feet long, with about 2.50 cubic feet or about 19 gallons of this solution filling it to a depth of about six inches, giving ample cross-sectional area for immersed travel of the wire beneath sheaves 21 and 22, under the surface of the solution in tank 18.

In practice the amperage passing through tank 18 slowly drops, and by refreshing the concentrations of chromic and sulfuric acid in tank 18, this current should be maintained between 50 and 75 amperes in the ten-foot tank 18 shown in FIGURE 2. When the anodic cleaning current in tank 18 drops to 40 amperes or below, the plastic applied in coating unit 28 may not adhere properly to the wire 10c. The same is true when this current rises to 90 amperes or more for the approximate ten-foot length of wire traveling through tank 18. The preferred range of 50 to 75 ampere currents is believed to reflect the optimum concentrations of the chromic and sulfuric acids providing the most effective coating of the chromium-copper film on the wire 10a, which apparently occurs while the wire travels from exit sheave 22 toward the exit end of cleaning tank 18.

The following examples of steel wire products provided with highly successful coatings of plastic or of metal through the processes of this invention will serve to illustrate the use of these processes for applying different types of coatings.

Example I

20 gauge hot galvanized AISI Grade C1008 low carbon steel wire, 0.0348 inch in diameter, is drawn in continuous commercial coating operation shown in FIGURE 2 through a diamond die block 16 having a nominal internal diameter of 0.0305 inch, with water as the lubricant in die-box 14. The wire passes through the anodic cleaning



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bath in tank 18, of chromic acid and sulfuric acid as specified above, with free metallic copper blocks 20 immersed therein, and with the current flow through bath 18 maintained between 50 and 75 amperes while approximately a ten-foot length of the traveling wire is immersed therein. Following a water rinse in bath 23, the wire is air dried and preheated in unit 27, and it travels through coating chamber 32 of heated polymer coating unit 28, where a molten nylon layer adheres to the surface of the wire. After air-cooling and water cooling in bath 33, the wire is wiped with a silicon protective wax coating and coiled on accumulator block drum 39, all as shown in FIGURE 2. Final commercial wire diameter may be selected to be 0.0305", 0.0320", 0.0330" or 0.0348".

## Example II

In the production line shown in FIGURE 3, a hot galvanized AISI Grade C1008 low carbon steel wire, 0.0410 inch in diameter is drawn in continuous operation through a cold drawing diamond die with a nominal internal diameter of 0.037 inch. The wire is wrapped twice around draw block 17 to provide tensile loading for cold drawing in die block 16, and is then wrapped twice around the sheaves 21 and 22 for two passes through cleaning tank 18, which contains the same cleaning-coating solution specified in Example I. The wire then passes through two water rinses, bath 23 (FIGURE 2) and bath 41 (FIGURE 3), and then, bypassing dipping tank 49, the wire passes through the multi-compartment plating tank 56 containing an aqueous solution of aluminum sulfate and zinc sulfate in the following proportions:

	Grams
Aluminum sulfate -----	1000
Zinc sulfate -----	500
Water -----	2000
Total -----	3500

During its passage through plating tank 56, the wire is exposed to a plating current of about 8 amperes at a voltage of from about 2 to about 4 volts D.C. The wire then passes directly to cold drawing die-box 63 containing as a drawing lubricant the following solution:

	Grams
Stannous chloride -----	120
Caprolactam monomer -----	120
Water -----	945
Total -----	1185

The diamond cold drawing die has a nominal internal diameter of 0.0320 inch, and the final drawing operation therein produces wire of that diameter with a cold drawn aluminum-zinc alloy coating plated thereon having an attractive "silvery" color. The caprolactam is apparently polymerized to some extent by the heat and pressure of the final cold drawing operation, giving a tough protective outer film on the finished wire.

## Example III

Under all of the same conditions specified in Example II above, the rinse baths of pure water were replaced by two dipping baths containing the plating solution of aluminum sulfate and zinc sulfate specified in Example II, with no plating current applied to these preliminary dipping baths. This preliminary dipping in the plating solution apparently forms a conductive film on the outer surface of the wire, directly over the chromium-copper film applied in the anodic cleaning bath 18, for in this Example III, with all other conditions being unchanged, plating current was observed to rise to an average of 15 amperes, giving an even more "silvery" appearing final color on the finished wire.

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## Example IV

Under all of the same conditions specified in Example II above, a bright, ungalvanized steel wire of the same diameter was passed through all of the treatment steps there specified, using two plain water rinse baths 23 and 41, and thence through a dipping bath in tank 49 comprising undiluted 45% copper fluoborate, sold by Harstan Chemical Corporation, after which the wire passed through plating tank 56 containing undiluted 40% zinc fluoborate as a plating electrolyte. This process produced a zinc-plated or galvanized wire apparently having a copper containing film between its outer zinc coating and the chromium-copper film applied in the anodic cleaning tank 18, for oven-heating of the resulting wire for five minutes darkens the "silvery" color of the wire, making it "golden" in color, suggesting that the pressure and heat generated by the cold working occurring during the final cold drawing operation supplemented by this additional oven-heating has converted the copper and zinc films in combination into a film of brass or similar alloy, providing an unusually tough, attractive coating on the steel wire.

## Example V

Under all of the conditions specified for Example IV above, the use of different electrolytes in different compartments of plating tank 56 produces even darker golden color in the resulting wire without the need for oven-heating. Thus passing the wire through one compartment of tank 56 filled with 45% copper fluoborate, with a copper anode block 58 immersed therein, followed by three successive compartments filled with 40% zinc fluoborate with zinc anode blocks 59, 61 and 62, with electroplating voltage source 54 adjusted to supply a plating potential of 5 volts at heavy plating current figures in the neighborhood of 40 amperes, produced golden-colored wire with a copper-zinc alloy plated and cold drawn thereon over the initial chromium-copper film applied in the anodic cleaning bath, giving a highly useful and unusually attractive wire for many different utilitarian, decorative and ornamental purposes.

## Example VI

Excellent results have also been achieved with the conditions specified in Example V above, but with the same electrolyte solution in all compartments of plating tank 56, comprising:

	Grams
Copper fluoborate -----	1000
Zinc fluoborate -----	1000
Total -----	2000

In this instance, anode blocks 58 and 59 were metallic copper blocks, and anode blocks 61 and 62 immersed in downstream compartments of tank 56 were metallic zinc blocks. During the rapid passage of the wire through plating tank 56, with plating voltage maintained between 4 and 5 volts and plating current between 35 and 40 amperes, the plated coating is initially rich in copper, and finally rich in zinc near its outer surface.

As shown in the foregoing examples, any size of wire may be treated by the coating processes of this invention. Standard wire sizes from 18 gauge to 22 gauge wire are regularly coated thereby in commercial operation, applying coatings ranging in thickness from 0.0002" to 0.0060" of nylon, epoxy, acrylics, polyethylene or polypropylene, or of aluminum-zinc alloys, copper-zinc alloys, or other protective metals or alloys, and all of these coatings are bonded with unusual firmness and tenacity to the underlying metal substrate, apparently by the action of the chromium-copper film applied during the anodic cleaning bath in tank 18.

While the objects of the invention are efficiently achieved by the preferred forms of the invention de-



scribed in the foregoing specification, the invention also includes changes and variations falling within and between the definitions of the following claims.

What is claimed is:

1. A process for coating a metal substrate which comprises the step of anodically cleaning the substrate and depositing a chromium- and copper-containing film upon said substrate by subjecting the substrate to an anodic aqueous cleaning bath of dilute chromic acid containing a small amount comprising not more than 2% of sulfuric acid and also containing a catalytic agent in the form of metallic copper placed in said bath in solid form and released into the solution through its reaction with the sulfuric acid.

2. A process for treating a metal substrate comprising the step of immersing the substrate in an aqueous cleaning bath of dilute chromic acid containing a small amount comprising not more than about 2% by weight of sulfuric acid and also containing at least one body of solid metallic copper immersed therein, while connecting said substrate to the positive terminal of a source of D.C. anodic cleaning potential whose negative terminal is also connected in electrically conductive relationship with said solid metallic copper.

3. The process defined in claim 2 wherein the substrate is an elongated continuous metallic member traveling continuously past consecutive treatment stations where the substrate passes successively through the anodic cleaning bath and through subsequent treatment stages.

4. The process defined in claim 2, further including successive treatment stages including rinsing, air drying, heating and molten polymer coating operations.

5. The process defined in claim 2, further including successive treatment stages including dipping in aqueous solutions of metallic salts.

6. The process defined in claim 5 wherein the metallic salts are aluminum sulfate and zinc sulfate, whereby a combined film containing both aluminum and zinc is deposited on the surface of the metal substrate.

7. The process defined in claim 2, further including successive treatment stages including electroplating in electrolytes composed of aqueous solutions of metallic salts, producing plated metallic film on the substrate.

8. The process defined in claim 7, further including a subsequent treatment step in which the plated metallic film and the underlying metal substrate are both subjected to cold working.

9. The process defined in claim 3 wherein the substrate is a continuous metal wire.

10. The process defined in claim 9 wherein the substrate is a continuous hot galvanized steel wire.

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