Oct. 20, 1953 H. A. TOULMIN, JR 2,656,284

METHOD OF PLATING ROLLED SHEET METAL

Filed Sept. 7, 1949

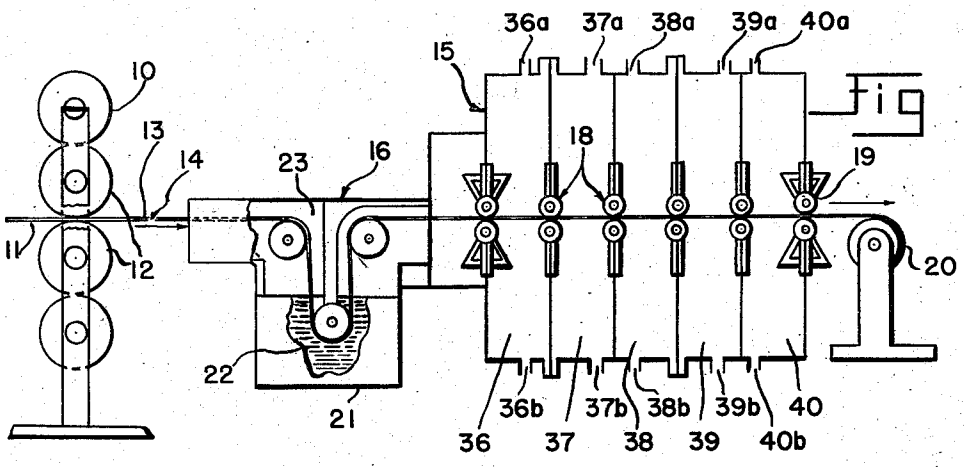


Fig 1

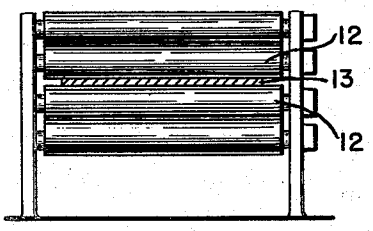


Fig 2

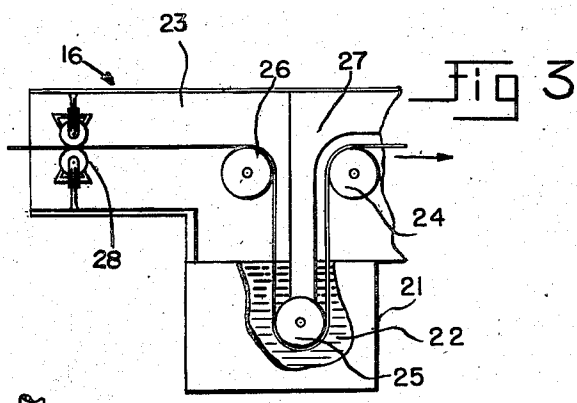


Fig 3

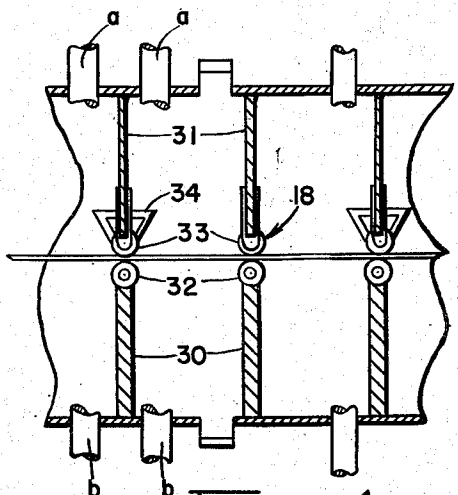


Fig 4

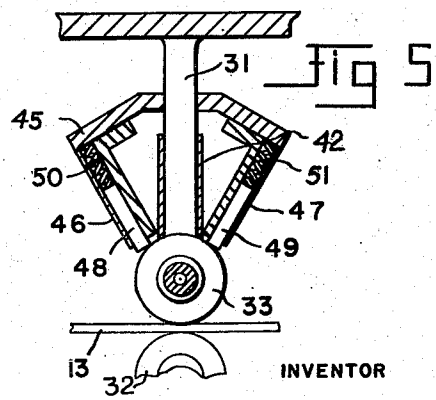


Fig 5

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Patented Oct. 20, 1953

2,656,284

UNITED STATES PATENT OFFICE

2,656,284

METHOD OF PLATING ROLLED SHEET METAL

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Application September 7, 1949, Serial No. 114,320

6 Claims. (Cl. 117—50)

1

This invention relates to the art of deposition of metals. More particularly, it relates to the plating of metals on continuously moving hot metal strip and apparatus for carrying out the process.

In the process of forming steel sheet, one method utilized is the hot rolling of ingots. The ingot is formed by casting and rolling to a slab size of 3 to 6 inches in thickness and of suitable width for charging into a reheating furnace where it is brought to a temperature of about 2200 to 2300° F.

The heated ingot then is passed to thickness reducing mills where it passes through a roughing train and a finishing train. These mills consist of multiple rollers and a number of roll stands depends upon the pressure which it is desired to exert. Roughing stands are usually four high and finishing stands are generally four to eight high.

If the rough down is accomplished in a reversing universal mill, the bar usually goes through a scale breaker and a high pressure spray and then into the four high hot strip stands.

In general, the finishing temperature varies from 1300 to 1600° F. and must be controlled to provide the desired mechanical properties.

In the finishing, strip bars of from 8 to 12 inches wide and about ¾ inch in thickness are heated in a pair furnace to about the above mentioned 1300 to 1600° F.

Pairs of bars are withdrawn from this furnace and rolled singly to a predetermined thickness. This rolled metal is then matched and rolled in pairs.

At the time of matching, the pairs are reheated in a sheet furnace and then are rolled to the desired degree of thinness.

As this thin metal sheet issues from the last stand of the finishing train, it is at a temperature in approximately the range of 1000 to 1200° F.

During the cooling operation the hot metal must be protected from the atmosphere in space consuming complicated equipment in order to avoid oxide formation, which both destroys the appearance and adds another step to the cleaning operation in order to prepare the metal for plating.

The products from this hot strip rolling operation often require additional treatment to produce better and smoother surface. For a large number of uses, the products must be surface smoothed to receive protective coating such as electrolytically deposited chromium.

It is an object of this invention to overcome

2

the disadvantages and limitations of the processes known heretofore.

It is also an object of this invention to produce plated rolled sheets in a relatively inexpensive manner.

It is a further object of the invention to provide a process which is of lower operating cost because it utilizes the heat of the metal as it issues from a rolling mill for the useful purpose of plating, whereas this heat normally presents a cooling problem and is a troublesome factor.

It is another object of the present invention to provide a protective coating formed on the metal while still hot which will protect iron against oxide formation.

It is a still further object of this invention to provide metal sheet with a variety of relatively inexpensively applied protective metal coatings which are not deposable by electrolytic methods.

It is another object of the present invention to provide a process wherein sheet metal as it issues from the rolling mill may be continuously plated on both sides.

Another object of this invention is to provide simplified apparatus for carrying out the above process.

Other and more specific objects and advantages will be apparent to one skilled in the art as the following description proceeds.

In brief, this invention comprises continuously passing sheet issuing from a hot rolling mill through a chamber where the heat of the metal is utilized to decompose metal-bearing gases and to deposit a protective coating. In this way, at least a portion of the heat in the metal is utilized instead of being dissipated.

Further, a coating is deposited which simplifies cooling through the critical temperature range for oxide formation because the iron is no longer exposed.

It will also be recognized that the process permits depositing an adhering protective metal coating, such as tungsten, which cannot be deposited electrolytically from liquid baths.

In sequence, the plate is subjected preferably to a reducing atmosphere, although this step is optional, plating with metal and annealing to impart ductility.

The plating operation may be divided into a preliminary flash coating with metal and a finish plating operation in which event an adhesion anneal or heating is interspersed between the two coating operations.

One of the factors important to the successful operation of the prefererd form of apparatus

hereinafter described in detail is control of gas pressure in each of the segments of the housing.

In order to insure against leakage of plating gases from the plating chamber or compartment and still have openings in the partition walls for continuous passage of metal sheet, it is necessary to maintain a metal-vapor free gas atmosphere at a slightly higher gas pressure in the housing segments or compartments preceding and succeeding the plating chamber.

The leakage of inert gas into a plating chamber is limited to small quantities by having apertures in the partition wall of a width providing only a loose sliding fit with the metal sheet passing therethrough and by keeping the pressure differential small.

It will be recognized that the inert gas leaking into the plating chamber is not a harmful operation because the metal-bearing gases are usually diluted with an inert gaseous medium and the gas decomposing reaction in the plating chamber produces relatively inert decomposition products such as carbon monoxide.

In the process a stream of gaseous material is brought into contact with the hot metal plate. The gaseous atmosphere may be formed by mixing an inert gas with the vapors of a volatile metal compound or by atomizing a liquid metal compound into a blast of hot inert gas or other equivalent method.

Carbon dioxide, helium, nitrogen, hydrogen, the gaseous product of controlled burning of hydrocarbon gases free of oxygen, and the like, have been utilized as a carrier medium or inert gas medium.

In some instances the use of hydrogen is preferred as, for example, in a first compartment of the housing where its ability to act as a reducing agent may be put to advantage to remove any oxide film on the surface of metal sheet.

Metals to be deposited may be introduced as gaseous metal carbonyls or vaporized solutions of certain of the metal carbonyls in readily vaporizable solvents (for example, petroleum ether), also nitroxyl compounds, nitrosyl carbonyls, metal hydrides, metal alkyls, metal halides, and the like.

Illustrative compounds of the carbonyl type are nickel, iron, chromium, molybdenum, cobalt, and mixed carbonyls.

Illustrative compounds of other groups are the nitroxyls, such as copper nitroxyl; nitrosyl carbonyls, for example, cobalt nitrosyl carbonyl; hydrides, such as antimony hydride, tin hydride; metal alkyls, such as chromyl chloride; and carbonyl halogens, for example, osmium carbonyl bromide, ruthenium carbonyl chloride, and the like.

Each material from which a metal may be plated has a temperature at which decomposition is complete. However, decomposition may take place slowly at a lower temperature or while the vapors are being raised in temperature through some particular range. For example, nickel carbonyl completely decomposes at a temperature in the range of 375° F. to 400° F. However, nickel carbonyl starts to decompose slowly at about 175° F. and therefore decomposition continues during the time of heating from 200° F. to 380° F. A large number of the metal carbonyls and hydrides may be effectively and efficiently decomposed at a temperature in the range of 350° F. to 450° F. When working with most metal carbonyls we prefer to operate in a temperature range of 375° F. to 425° F.

Maintenance of the metal sheet at temperatures in the general decomposition range is easily accomplished by guiding the metal sheet in timed sequence through a unit where the time for radiation and loss of heat is readily controlled and then directly into the plating apparatus.

For anneals between and after the plating operation the metal sheet may be heated by causing the metal plate to conduct electrictiy or to be heated by induction or other suitable means.

When annealing temperatures, which are considerably higher than plating temperatures, i. e. in the range of 800 to 1200° F., are to be used, the operation is preferably carried out by causing the metal sheet to conduct electricity. This generally consists of impressing upon terminals contacting the metal sheet a voltage sufficient to bring the sheet to a red heat.

The lower temperature of the plating area is then accomplished by placing an electrical shunt in parallel with the plating zone. In this way the amount of current passing in the metal sheet is reduced and as a result its temperature quickly lowers to a predetermined range.

With hot metal issuing from a finishing mill there is seldom any need to employ a preparatory surface cleaning operation. However, if one is found necessary conventional methods may be used.

The invention will be more clearly understood from the following description of one embodiment of the apparatus and its mode of operation.

In the drawings:

Figure 1 is a diagrammatic illustration of a complete plate forming and plating unit;

Figure 2 is a vertical front view diagrammatically showing the rollers of a stand and metal being rolled;

Figure 3 is an enlarged sectional view diagrammatically showing the seal used at either the inlet or outlet end of the housing for the plating unit;

Figure 4 is a sectional view diagrammatically illustrating the partition unit separating the housing into segments; and

Figure 5 is a vertical sectional view of the flexible upper leg of the partition divider which yields thus permitting the equipment to accommodate any metal sheet thickness.

Referring to the drawings, there is shown a four high stand **10** of the finishing train of a rolling mill. A strip of metal **11** composed of paired sheets of iron which have been heated to about 1300° F. in a pair oven (not shown) is illustrated being fed between the middle rollers **12** of the stand **10** and issuing as a sheet **13**, of desired reduced thickness.

The sheet **13** after suitable delay for cooling about 600 to 700° F. indicated at **14** by the broken strip, enters a housing **15**. Entrance to the housing **15** is made through a seal **16**. The rolled plate within the housing **15** passes through the partition units **18** and is drawn out through a seal **19** which is of roller construction or a seal similar to seal **16**. The strip is wound on suitable spools or reels **20** or otherwise accumulated.

Seal **16** is more fully illustrated in Figure 3 and consists of a trough **21**. This trough is adapted to be filled with a fluid **22**, such as mercury, low melting point eutectic fusible alloys, or equivalent fluid. Mounted on the trough **21** is a support **23**. Support **23** carries three rollers **24**, **25** and **26** mounted on ball bearings for free action.

Support **23** is composed of a vertical portion **27** adapted to extend into the mercury bath and

provides at its bottom end the mounting for roller 25.

The support 23 provides at its extremity the mounting for roller 24. The leftwardly extending portion of support 23 forms a housing within which roller 26 is free to rotate.

If desired guide rollers 28 may be utilized.

Partition elements 18, as shown more in detail in Figures 4 and 5, consist of lower and upper wall members 30 and 31 upon which are mounted through suitable brackets rollers 32 and 33, respectively.

Inasmuch, as the hot metal strip must be supported during its travel, rollers 32 are mounted atop the bottom half of partition wall 30 in fixed position. To provide flexibility in thickness of sheet that may be handled roller 33 is affixed to a movable mounting 34. One version of this mounting adapted to provide gas tight engagement is shown in more detail in Figure 5.

In this type mounting providing sealing engagement wall 31 acts as a support. Slidably engaging wall 31 is a guide 42. This guide 42 supports through suitable brackets bearings for roller 33.

Wall 31 is also the guide for a bracket 45. Bracket 45 is formed with two channeled leg members 46 and 47. In the legs are held members 48 and 49 yieldingly urged into engagement with the roller 33 by springs 50 and 51, respectively.

If desired, as an additional precaution against leakage of gas, suitable gasketing material may be affixed. Also, if electrical contact is desired suitable conduit may be positioned on wall 31 and attached to a terminal of a brush contact with any of said rollers 33.

Referring again to Figure 1, housing 15 may be divided by partition units 18 into a number of segments, in this case illustrated with five segments 36 to 40, inclusive.

Each segment or compartment is provided with inlet and outlet conduits, as for example 36*a* and 36*b*.

In brief, the operation of the apparatus is as follows:

Hot rolled sheet 13 issuing from between the rollers 12 after suitable delay move through seal 16 by passing over roller 26 and down through the mercury.

The hot rolled sheet turns upward after passing below pulley 25 and passes over pulley 24. The hot rolled sheet then traverses the first compartment 36 where it is in contact with an inert gas atmosphere.

This brings the sheet into the flash coating chamber. The sheet then passes through another partition 18 and is energized by contact with rollers 33 having an electrical connection for heating to annealing temperature.

The hot rolled sheet passes entirely through the housing 15 and its partitioning element 18 until it emerges through the outlet seal 19. The coated sheet is then accumulated on reel 20.

Gas is circulated through each compartment and, under certain circumstances, through compartments joined in series. For example, plating gas may be circulated through the plating compartments 37 and 39 in series, while inert gas alone may be circulated in compartments 36, 38 and 40 in series.

The gas is generally circulated in counter-current flow to the direction of movement of the sheet being plated. To this end gas is fed to each compartment through an inlet indicated *a* near the point of plate egress from the compartment and an outlet indicated *b* near the point of ingress into the compartment.

When using a five segment apparatus for coating described in connection with the drawing, plating gases are excluded from the non-plating sections or compartments by passing through these compartments one or more of the above mentioned inert gases, at rates in the range of 10 to 20 cubic feet per hour per cubic foot of plating chamber.

In the plating chamber gas flow of mixed gas containing inert gas, such as nitrogen mixed with volatile metal compounds, is at a gas rate in the range of 2 to 5 cubic feet per hour per cubic foot of plating chamber.

In the plating of nickel upon 32 inch wide sheet SAE 4340 of approximately .025 inch in thickness, the following conditions may be maintained:

The temperature of the sheet entering the plating chamber may be approximately 425° F., for the anneals between plating and following the last plating step, the rolled sheet may be heated to approximately 1000° F., rate of flow of carbon dioxide gas through the annealing compartments in series may be approximately 20 to 40 cubic feet of gas per hour per cubic foot of chamber space.

Rate of flow of gas through the plating compartments may be approximately 10 to 30 cubic feet per hour per cubic foot of chamber space, with nickel carbonyl vapors being present when it is desired to deposit a nickel plate in the ratio of approximately 10 ounces of carbonyl per cubic foot of carbon dioxide gas passed through the plating chamber.

It will be understood that while the method and apparatus disclosed and described herein illustrate a preferred form of the invention, modification can be made without departing from the spirit of the invention, and that all modifications that fall within the scope of the appended claims are intended to be included herein.

For example, plating is accomplished in the above apparatus on both sides of the paired sheets. However, when these sheets are separate it will at once be recognized that the individual sheets are only plated on one side. If the paired sheets, however, are split before plating, it will at once become apparent that each individual half sheet can be plated on both sides.

I claim:

1. A process of continuously plating a moving hot metal sheet as delivered from a mill which comprises the steps of guiding said hot metal sheet therealong while heated to a temperature between about 1300 and 1600° F., cooling the same under nonoxidizing atmospheric conditions, said metal sheet being cooled to a temperature which is sufficient to cause decomposition of a heat-decomposable metal vapor compound brought in contact therewith, subjecting said hot moving sheet to a plurality of gaseous metal plating treatments, said gaseous metal plating treatments comprising exposing said moving hot sheet in a plating chamber to a gaseous mass at least a portion of which consists of a heat-decomposable metal vapor compound, said plating chamber having chambers adjacent thereto which are kept under slightly higher gas pressure than in said plating chamber, said sheet being maintained at a temperature sufficient to cause decomposition of said heat-decomposable metal vapor compound and deposition of the

metal constituent thereof on said moving hot metal sheet.

2. A process of continuously plating a moving hot metal sheet as delivered from a mill which comprises the steps of guiding said hot metal sheet therealong while heated to a temperature between about 1300 and 1600° F., cooling the same under non-oxidizing atmospheric conditions, said metal sheet being cooled to a temperature which is sufficient to cause decomposition of a heat-decomposable metal vapor compound brought in contact therewith, subjecting said hot moving sheet alternately to a plurality of gaseous metal plating and heating treatments, said gaseous metal plating treatment comprising subjecting said sheet in a plating chamber to a heat-decomposable gaseous metal compound, said plating chamber having chambers adjacent thereto which are kept under slightly higher gas pressure than in said plating chamber, said sheet being maintained heated at a temperature sufficient to cause decomposition of said gaseous metal compound and deposition of the metal constituent thereof on said hot sheet, said plating and heat treatments being carried out under non-oxidizing atmospheric conditions.

3. A process of continuously plating a moving hot metal sheet as delivered from a mill which comprises the steps of guiding said hot metal sheet therealong while heated to a temperature between about 1300 and 1600° F., cooling the same under non-oxidizing atmospheric conditions, said metal sheet being cooled to a temperature which is sufficient to cause decomposition of a heat-decomposable metal vapor compound brought in contact therewith, subjecting said hot moving sheet to a plurality of gaseous metal plating treatments, said gaseous metal plating treatments comprising continuously exposing said hot sheet in a plating chamber to a continuously moving gaseous material composed of carbon dioxide and a heat-decomposable gaseous metal compound, said plating chamber having chambers adjacent thereto which are kept under slightly higher gas pressure than in said plating chamber, and wherein said moving metal sheet being maintained at a temperature sufficient to cause decomposition of said gaseous metal compound and deposition of the metal constituent thereof on said hot moving sheet.

4. A process of continuously plating a moving hot metal sheet as delivered from a mill which comprises the steps of guiding said hot metal sheet therealong while heated to a temperature between about 1300 and 1600° F., cooling the same under non-oxidizing atmospheric conditions, said metal sheet being cooled to a temperature which is sufficient to cause decomposition of a heat-decomposable metal vapor compound brought in contact therewith, subjecting said hot moving sheet in a plating chamber and while heated to a temperature sufficient to cause decomposition of said gaseous metal compound circulated in contact therewith and deposition of the metal constituent thereof on said hot moving sheet, said plating chamber having chambers adjacent thereto which are kept under slightly higher gas pressure than in said plating chamber, thereafter subjecting said sheet to a heat treatment under non-oxidizing atmospheric conditions as the same is moved therealong, said heat treatment of the moving sheet being at a temperature substantially higher than that for causing decomposition of said gaseous metal compound.

5. A process of continuously plating a moving hot metal sheet as delivered from a rolling mill which comprises the steps of guiding said hot metal sheet therealong while heated to a temperature between about 1300 and 1600° F., cooling the same under non-oxidizing atmospheric conditions, said metal sheet being cooled to a temperature which is sufficient to cause decomposition of a heat-decomposable metal vapor compound brought in contact therewith, subjecting said hot moving sheet to a plurality of gaseous metal plating treatments, said gaseous metal plating treatments comprising exposing said moving hot sheet in a plating chamber to a continuously moving gaseous mixture of carbon dioxide and nickel carbonyl, said plating chamber having chambers adjacent thereto which are kept under slightly higher gas pressure than in said plating chamber, said sheet being maintained at a temperature sufficient to cause decomposition of the nickel carbonyl and deposition of nickel on said hot metal sheet as the same is continuously moved therealong.

6. A process of continuously plating a moving hot metal sheet as delivered from a rolling mill which comprises the steps of guiding said hot metal sheet therealong while heated to a temperature between about 1300 and 1600° F., cooling the same under non-oxidizing atmospheric conditions, said metal sheet being cooled to a temperature which is sufficient to cause decomposition of a heat-decomposable metal vapor compound brought in contact therewith, subjecting said hot moving sheet in a plating chamber to a heat-decomposable gaseous metal compound at a temperature sufficient to cause decomposition of the gaseous metal compound and deposition of the metal constituent thereof on the hot metal sheet, subjecting the resultant metal coated hot sheet to a temperature substantially above that required to decompose said gaseous metal compound and while maintaining said sheet under non-oxidizing atmospheric conditions, and thereafter cooling said sheet to a temperature sufficient to cause decomposition of a gaseous metal compound and contacting said cooled metal sheet in a plating chamber with a heat-decomposable gaseous metal compound whereby decomposition of the gaseous metal compound and deposition of the metal constituent thereof on said heated precoated moving sheet is effected, said plating chambers having chambers adjacent thereto which are maintained at a slightly higher gas pressure than in said plating chambers.

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