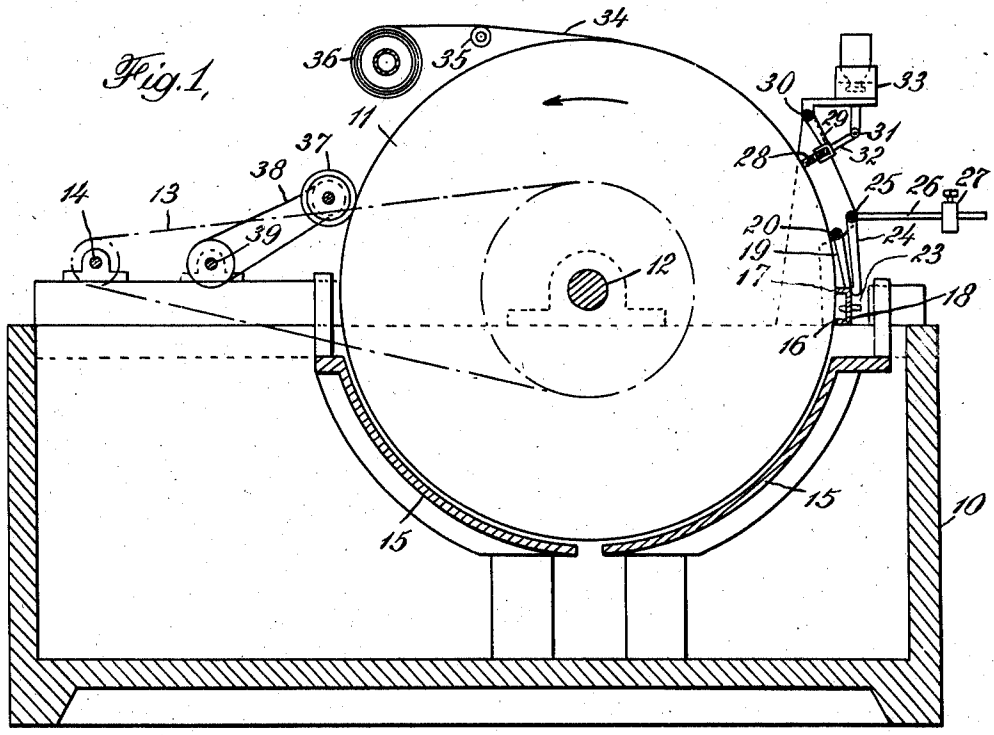
July 20, 1943. H. C. MACAN 2,324,859

PROTECTING ELECTRODEFOSITED METAL SURFACES

Filed April 30, 1940

Fig. 1.



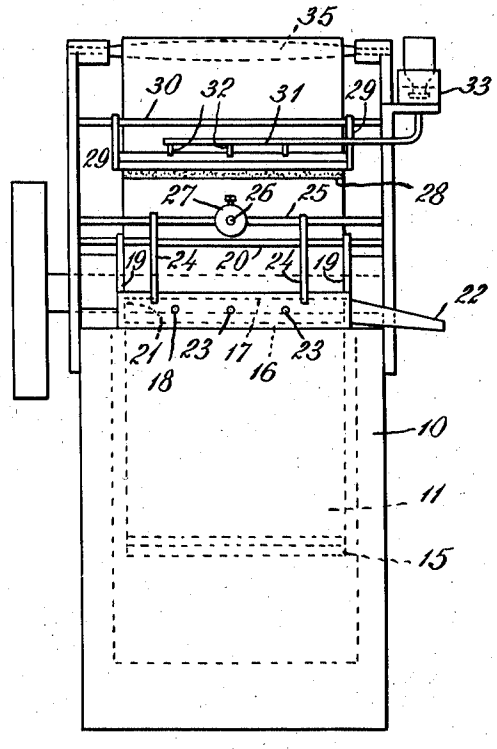


Fig. 2.

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Patented July 20, 1943

2,324,859

UNITED STATES PATENT OFFICE

2,324,859

PROTECTING ELECTRODEPOSITED METAL SURFACES

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Application April 30, 1940, Serial No. 332,553

1 Claim. (Cl. 204—13)

This invention relates to the protection of electrodeposited metal surfaces and is concerned more particularly with the provision of an improved method for preventing surface discoloration of sheet metal produced by electrodeposition. The invention also provides an improved electrodeposited metal sheet which is markedly more resistant to discoloration than heretofore known electrodeposited metal sheets. This application is a continuation in part of my earlier application Serial No. 273,011, filed May 11, 1939.

In the manufacture of sheet metal by electrodeposition, a layer of the metal is deposited electrolytically from a suitable electrolyte on to the surface of a cathode, such as a rotating drum cathode partially immersed in the electrolyte. The cathode with the metal deposited thereon is then withdrawn from the electrolyte, as by rotating the cathode drum to bring the deposited metal above the surface of the electrolyte, and the deposited metal is stripped from the cathode in sheet form.

A process of this nature for the production of sheet copper has been in use for some time, using a rotating drum cathode partially immersed in an aqueous electrolyte containing sulphuric acid and copper sulphate. Copper sheets of considerable widths (depending upon the width of the cathode face of the drum) and of thickness ranging from vary thin foil to moderately heavy sheet (depending upon the speed with which the cathode drum is rotated) are produced by this process. Heretofore, however, much difficulty has been experienced in preventing discoloration of the surface of the copper sheet so produced, particularly of the surface which, during deposition, is in contact with the electrolyte. This surface of the sheet generally presents a matt or dull appearance, due to the fact the innumerable minute protuberances of copper are formed thereon during electro-deposition of the sheet on the cathode. In the aggregate these minute protuberances provide an extremely large exposed area, which apparently makes this matt surface of the sheet readily subject to the reactions which cause discoloration. Discoloration of this matt surface of the sheet is in some cases so severe as to penetrate through the sheet and appear on the other side thereof.

The other surface of the sheet, that is, the surface which, during deposition, is in contact with the cathode drum, is generally bright in appearance, owing to the fact that the cathode surface is kept polished. This bright surface of the sheet is much less subject to discoloration than the matt surface.

Discoloration appears to be due to chemical reaction of the electrodeposited metal with oxygen and with substances such as sulphur compounds present in the atmosphere, and often is accompanied by physical deterioration of the sheet, such, for example, as embrittlement and even decrepitation of the embrittled sheet. Attempts have been made to avoid discoloration and the frequently accompanying deterioration of the metal by taking great pains to insure complete washing of the acid and other ingredients of the electrolyte from the surface of the sheet after its formation, but these attempts have met only with indifferent success.

The present invention provides a method for preventing such discoloration and deterioration of electrodeposited sheet metal which has proven much more effective than the methods heretofore proposed. Briefly, the new method comprises washing the sheet, advantageously with water, before it has become discolored, drying the washed sheet, and applying to the dried sheet a coating composition comprising a volatile liquid vehicle having good wetting properties and carrying in solution a small amount of a substantially non-volatile inert organic compound capable of forming an extremely thin, substantially continuous protective film over the surface of the metal upon evaporation of the liquid. Washing of the sheet before it has become discolored is important in order to remove electrolyte adhering to the sheet after its withdrawal from the electrolytic cell. If such electrolyte is permitted to remain on the sheet for any considerable period of time, it promotes discoloration of the sheet. It is important to dry the sheet after washing so that the subsequently applied protective film will be substantially continuous and give effective protection to the sheet. It is also important that the volatile liquid vehicle have good wetting properties so that it will spread quickly and evenly over the surface of the sheet and thereby insure formation of a uniform protective film of the non-volatile inert material.

Electrodeposited metal sheet treated in accordance with the invention is characterized by having at least one of its surfaces coated with an extremely thin, substantially continuous protective film of a substantially non-volatile inert organic compound which protects the underlying metal from discoloration, and which is so thin that the treated sheet is not greasy to the touch.

It is even possible, in accordance with the invention, to produce a sheet having a coated surface which will receive and bond to an adhesive despite the presence of the protective coating, and which will receive an ink impression fully as well as an untreated sheet.

As indicated above, the matt surface of the sheet is particularly susceptible to discoloration, and protection of this surface in accordance with the procedure of the invention is therefore particularly desirable. The entire treatment of this surface of the sheet, including the successive steps of washing, drying, and application of the coating composition, is advantageously carried out while the sheet is still on the cathode drum between the point of emergence of the sheet from the electrolyte and the point at which the sheet is stripped from the drum.

The invention will be better understood from the following description of a preferred embodiment as applied to electrodeposited copper sheet, considered in connection with the accompanying drawing, in which

Fig. 1 is a diagrammatic cross-section through an apparatus suitable for use in carrying out the method of the invention; and

Fig. 2 is an end view of the apparatus shown in Fig. 1.

The apparatus comprises a tank **10** containing a suitable electrolyte, such as a sulphuric acid solution of copper sulphate, preferably at an elevated temperature of about 130° F. to 140° F. A rotating drum cathode **11** partially immersed in the electrolyte is mounted for rotation about its longitudinal axis on a shaft **12**. The drum **11** is rotated in the direction of the arrow by means of a chain **13** engaging a sprocket on a suitable drive shaft **14**.

Anodes **15** curved to conform with the cylindrical surface of the drum cathode **11** are mounted in the tank **10** below the surface of the electrolyte in spaced relation with the surface of the cathode. Suitable electrical connections are made to the drum cathode and to the anodes for the purpose of causing copper to be deposited electrolytically from the electrolyte on to the surface of the cathode.

As the cathode drum rotates, the deposit of copper thereon is withdrawn from the electrolyte and is passed under a pair of spaced doctor blades **16** and **17** bearing against the exposed surface of the copper. The doctor blades, which may be of rubber, extend the width of the cathode face of the drum and are mounted on a back closure **18** pivotally supported by brackets **19** from a shaft **20**. The weight of the doctor blade assembly holds the blades **16** and **17** in contact with the copper. A closure member **21** is provided at one end of the doctor blade assembly between the back closure **18**, the blades **16** and **17** and the surface of the cathode drum, and a spout **22** is provided at the other end.

Water spray nozzles **23** suitably connected to a source of water under pressure (not shown) extend through the back closure **18** into the space within the doctor blade assembly.

A pressure arm **24** pivotally mounted on a shaft **25** bears against the doctor blade assembly. A lever **26** rigidly connected to the pressure arm **24** and carrying a weight **27** urges the pressure arm **24** against the doctor blade assembly in a manner to press the latter firmly against the exposed surface of the copper on the drum. The position of the weight **27** on the lever arm **26** is adjustable so as to permit adjustment of the force with which the doctor blade assembly is pressed against the copper.

During operation of the apparatus, water is sprayed through the nozzles **23** against the surface of the copper deposit between the doctor blades **16** and **17**. As the cathode rotates, the lower doctor blade **16** wipes electrolyte from the surface of the deposited copper, and the water introduced through the spray nozzles **23** washes the surface of the copper free of such electrolyte as is not wiped away. The upper doctor blade **17** dries the surface of the copper by wiping it substantially free of wash water. The arrangement of the two doctor blades, the back closure **18**, and the closure **21**, prevents wash water from running into and diluting the electrolyte. The wash water is withdrawn from the space between the doctor blades through the spout **22** at the end of the doctor blade assembly.

Substantially complete drying of the sheet, after the preliminary drying by wiping with the doctor blade **17**, is effected by evaporation of the small residual amount of wash water adhering to the sheet. Such evaporation is favored by the heat of the cathode drum, which in turn is heated by the electrolyte in which it is immersed.

The copper deposit on the drum cathode **11**, after being withdrawn by rotation of the cathode from the washing means, and after passing a short distance through the air to permit evaporation of residual wash water, passes under a felt doctor blade **28** pivotally mounted by means of a suitable bracket **29** on a shaft **30**. The weight of the bracket and the doctor blade **28** holds the latter in contact with the surface of the copper deposit.

The felt doctor blade **28** is kept moistened with the liquid used for coating the surface of the copper. A suitable device for this purpose comprises a manifold **31** having a plurality of short discharge pipes **32** feeding the liquid to the doctor blade **28**. Liquid is introduced into the manifold **31** from a suitable feed tank **33**.

After the copper has passed under the felt doctor blade **28** and received its coating, it is stripped in the form of a sheet **34** from the surface of the cathode by passage over a stripping roll **35**. In the case of very thin sheet copper, the stripping roll advantageously is of the type described and claimed in my co-pending application Serial No. 273,012, filed May 11, 1939. The copper sheet **34** passes from the stripping roll to a reel **36** onto which it is wound.

Rotation of the cathode brings the stripped surface thereof into contact with a polishing brush **37** just before reentry of the cathode surface into the electrolyte. The polishing brush **37**, which is rotated in contact with the cathode by means of a chain **38** engaging a sprocket on a drive shaft **39**, serves to maintain the surface of the cathode in suitable condition for the production of electrodeposited sheet.

The coating composition applied to the electrodeposited sheet after washing and drying comprises a volatile liquid vehicle having good wetting properties and carrying in solution an amount of a substantially non-volatile, preferably semi-transparent, inert organic compound, capable of forming an extremely thin, substantially continuous, protective film over the surface of the copper upon evaporation of the liquid. The vehicle should have good wetting properties because the felt doctor blade **28** by which it is applied to the surface of the copper cannot be relied upon to insure uniform and complete spreading of the liquid over the surface of the

copper. A liquid having good wetting properties will spread easily and so result in a uniform coating. The vehicle should also be sufficiently volatile so that it will dry fairly completely by evaporation in the short interval of time required for the copper to be passed from the felt doctor blade 28 to the take-up reel 36. This time, in the case of very thin sheet copper (which is produced by rotating the cathode drum 11 at a relatively high rate of speed), is very short, being of the order of only a few seconds. In the case of heavier copper sheets produced at relatively low drum speeds, the time interval is longer and high volatility of the liquid is not so important. It is not essential in all cases that the vehicle be evaporated completely by the time the sheet copper is wound on to the reel 38, but in general it is preferred that the sheet be substantially dry upon reeling. Hydrocarbon liquids, especially the lower boiling fractions, are preferred as coating solution vehicles, for such liquids in general possess good wetting properties and are adequately volatile, although other organic and inorganic liquids may be employed with success.

The non-volatile inert component of the coating composition may be any substance which is capable of forming a permanent, substantially continuous film over the surface of the metal sheet, and of protecting the sheet from discoloration. The material should, of course, be non-volatile so that the film which it forms will remain permanently on the sheet. It should be non-reactive with the surface of the metal to which it is applied. Preferably it should be substantially colorless so as not to impair the natural color of the sheet. It should be readily soluble in the vehicle so as to be spread thereby evenly over the surface of the sheet.

Numerous inert substances, mostly of an organic nature, are available for use as the non-volatile protective component of the coating solution. Waxy materials in general are particularly satisfactory. Paraffin wax, for example, has been used with marked success. Floor waxes may be used, although they are usually of a brownish color and tend to color the sheet correspondingly. For this reason they may be found undesirable, although they provide effective protection against normal discoloration and deterioration of the sheet. Various other waxes, such as beeswax, carnauba wax, and the like also may be employed. Resinous substances which are soluble in the vehicle and capable of forming a permanent film on the surface of the metal may be used with success. Drying oils (linseed oil, China-wood, and soy bean oil, for example) may be used in suitable liquid vehicles. The use of non-drying oils or other non-volatile permanently liquid substances, however, is not to be recommended, for the film formed by such oils or other substances is likely not to be very permanent, and are, moreover, apt to give the surface of the sheet an oily or greasy feel.

The quantity of waxy or other non-volatile protective substance dissolved in the liquid vehicle may vary considerably, but should be fairly small, for example, not more than 60 grams per liter or thereabouts. Such amounts of the protective substance dissolved in the vehicle do not make the sheet greasy to the touch, and even higher concentrations can be employed without serious objection for this reason. Such high concentrations, however, are no more effective than lower concentrations in providing protection against discoloration. In fact, such high concentrations of the protective substance may even impart a uniform though undesirable color to the sheet which it is intended to protect against discoloration from other causes. Twenty grams per liter or less is an adequate concentration of the protective substance in the vehicle for most purposes, and much lower concentrations even than this may be employed with complete success. For example, very satisfactory results have been obtained using concentrations of the protective substance in the vehicle of the order of 0.2 gram per liter.

A particularly satisfactory coating solution is a material known under the trade-name "Varsol." This is a volatile hydrocarbon liquid boiling between 307° F. and 396° F. and having an A. P. I. gravity of about 45°. It is generally taken as a separate fraction between the higher boiling gasoline fractions and the lower boiling kerosene fractions of petroleum distillates and is about 55% volatile at 350° F. and about 95% volatile at 392° F. It ordinarily contains, apparently as a commercial impurity, a very small amount (about 0.2 gram per liter) of non-volatile material which serves very well to protect electrodeposited sheet metal when the "Varsol" is spread thereon and allowed to evaporate. Hence commercial "Varsol" may be employed alone, or if desired it may be fortified by dissolving therein a small amount, say up to 20 grams per liter, of an inert wax such as paraffin wax. "Varsol" possesses excellent wetting properties (a drop of this substance on an area of 0.06 square inch spreads in one minute time to cover an area of about four square inches) and is adequately volatile. One gallon of unfortified commercial "Varsol" will coat about 20,000 square feet of the matt surface of electrodeposited copper sheet.

Electrodeposited copper sheet coated with "Varsol" is protected indefinitely from discoloration and deterioration, whereas sheets not so protected ordinarily discolor and deteriorate in about three weeks. The residual film left on the surface of the copper by the "Varsol" is so very thin as not to impair in any way the appearance of the copper. Neither does it affect the adhesion of glues or cements to the copper, nor impair the capacity of the metal to receive ink or paint.

Another material which has been employed with success in coating electrodeposited copper sheet is a product available under the trade name "Santomerse" from the Monsanto Chemical Company. "Santomerse" is a detersive agent comprising salts of a homologous series of substituted aromatic sulphonic acids, namely, alkylated aryl sulfonates, and may be obtained commercially in the form of a 30% aqueous solution. This commercial solution may be diluted with water, for example in the proportion of one part of the commercial 30% "Santomerse" solution to twenty parts of water, and when so diluted may be employed effectively as the coating solution for protecting the copper sheet against discoloration. "Santomerse" possesses excellent wetting properties and from this standpoint is entirely satisfactory for use in the present invention. Being an aqueous solution, however, its volatility is not very high and on this account it is not as satisfactory a material as "Varsol," particularly in coating very thin copper sheets produced at a high rate of speed.

Gasoline is another substance that may be employed in preparing coating solutions. Gasoline as it is commercially available ordinarily contains an insufficient amount of non-volatile

material to provide an effective coating on the metal sheet, but gasoline in which a small amount, from a fraction of a gram to ten or more grams per liter, of a wax or other suitable non-volatile inert organic compound has been dissolved may be employed successfully.

Carbon tetrachloride is still another liquid which may be used effectively as the vehicle for the coating solution. Commercial carbon tetrachloride contains insufficient non-volatile material to provide an effective coating on the metal sheet, but if a small amount of a suitable inert material is dissolved therein, the resulting solution is entirely satisfactory.

Kerosene may be employed alone for coating the metal sheet. Commercial kerosene contains an adequate amount of substantially non-volatile inert hydrocarbons to provide a coating on the metal sheet capable of protecting it against discoloration. The film left on the sheet coated with kerosene, however, is likely to be greasy to the touch, and objectionable for this reason.

Numerous other volatile liquids, both organic and inorganic in nature, are available and may be used in making up the coating composition.

Although the invention has been described above with particular reference to the protection of electrodeposited sheet copper, and especially the matt surface thereof, from discoloration and deterioration, it is understood that other electrodeposited metal sheets may likewise be protected in accordance with the invention, and that the coating composition may be applied in accordance with the invention either to the matt or to the bright surface of the sheet, or to both surfaces, as desired.

I claim:

In the manufacture of sheet copper by electrodeposition from a suitable electrolyte, the method of protecting a surface of the electrodeposited sheet from discoloration which comprises washing and drying the surface of the sheet to be protected after withdrawal thereof from the electrolyte, and thereafter applying to the dry surface a coating of a volatile liquid hydrocarbon having good wetting properties and sufficiently volatile to evaporate quickly and completely from the sheet and carrying in solution from about 0.2 to 60 grams per liter of a wax capable of forming upon evaporation of volatile liquid an extremely thin and substantially imperceptible protective coating over the surface of the sheet, said wax coating having the property of receiving and bonding to an adhesive.

HARRY C MACAN.