

1

2,859,145

COLD ROLLING OF STEEL

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The present invention relates to a method for improving the continuous cold rolling of ferrous strip stock and more particularly relates to a process which permits the elimination of the conventional oiling step prior to rolling and produces a smoother, flatter rolled strip than has been heretofore obtainable. The process includes the provision of a phosphate coating on steel strip stock moving through a conventional strip steel pickle line under conventional conditions and then cold rolling that treated strip.

It was early suggested in U. S. Patent No. 2,105,015 that the deformation of metal was facilitated by providing a phosphate coating on the metal surface prior to the deforming operation. It has also been suggested that the drawing of wire, bar stock, tubes and the like is made easier by phosphate coating the part to be drawn. To the best of our knowledge there has been no proposal of a process suitable for use in continuous cold rolling of steel strip stock.

Present day cold rolling processing of steel strip stock comprises preparing the roll surface for cold rolling and then cold rolling in a reversing mill or a multiple stand mill. Low carbon steel, silicon steel or other steel strip, which emerges from a conventional hot rolling mill usually has some residual rolling scale and corrosion products on its surface. The preparation for cold rolling normally includes processing the hot rolled strip to clean the surface by passing it through a pickle line of conventional form which may, for example, include in sequence one or more mineral acid dip stations, one or more water rinse stations and an oiling station. In certain instances where the mill scale is heavy, the pickle line may include mechanical abrading stations or alkali stations prior to the acid dip stations. The steel strip is continuously passed through these sequential stages and is recoiled after oiling to await the cold rolling operation. The rolling mill, whether reversing or multiple stand, operates at speeds and under conditions which make it impossible to feed directly from the pickle line to the rolling line. Because of this necessary but variable length delay between the pickling of the strip and its rolling, the corroding of the pickled strip becomes an important problem. It is for this reason that most pickle lines include a final oiling station. The oiling step is highly undesirable from the dual standpoints that it drips from the pickled coils, makes the working area slick, dirty and unsafe for workmen and that after cold rolling when the cold rolled strip is annealed the oil residue produces a surface coating of undesirable smut.

It will be apparent that in order to produce sufficient pickled steel strip to keep a cold rolling mill in continuous production, the pickle line must necessarily operate continuously and at relatively rapid speeds in order to be economic. Although actual speeds necessarily vary in different installations, pickle line speeds in the range of 150 feet per minute to 450 feet per minute are common. One of the difficulties in supplying a process for continu-

2

ously forming a phosphate coating on the strip steel moving through a pickle line is to provide a solution which will form the necessary coating in the limited time which is available for contact of the strip surface with the phosphate coating solution. For example, if the pickle line moves at 125 feet/minute a phosphate coating tank having a 25 foot length provides only about 10 seconds contact time for the strip. It will be apparent that as the pickle line speed increases, either the phosphate coating tank must be greatly lengthened or the coating solution must be adapted to act in a much shorter time than 10 seconds, for example in 3 to 8 seconds.

In the rolling of strip through a reversing mill or in a multiple stand mill, the most important objective is to produce rolled strip of uniform thickness or gauge having good surface finish. The speed of travel of a steel strip through a cold rolling mill will vary, reversing mills being generally slower than multiple stand mills. In order to be economic, the strip speed should be above about 600 feet/minute and preferably above about 1000 feet/minute with speeds as high as 5000-7500 feet per minute being obtainable on present day multiple stand rolling mill equipment. It will be appreciated that variations in gauge of the resulting strip can only be accomplished by varying the spacing between the rolls and at economic cold rolling speeds only extremely minor adjustments of the roll spacing can be made while the strip is passing through the rolls. In accordance with this invention it has been found that when variations in the weight or thickness of the phosphate coating on the surface of the strip exist, the rolling mill operator experiences difficulty in maintaining gauge. When the phosphate coating weight varies widely from point to point along the strip, attempts by the operator to correct for these variations may cause side slipping or ultimate ripping and tearing of the strip. When a thick portion is observed by the operator the roll pressure is increased in an attempt to hold gauge and as the thicker portion of the strip passes through the rolls the extra roll pressure causes the rolls to grab the following portion of the strip and thus cause ripping or tearing. This problem represents the most formidable difficulty which must be overcome in providing a continuous phosphate coating process for steel strip. It was further found that when using conventional phosphate coating solutions and normal delays in processing in the pickle line occurred, that portion of the steel strip in contact with the phosphate coating solution during the delay received a heavier, and thus thicker phosphate coating than other portions of the strip which passed through the solution at the normal pickle line speed. Normal operation of a pickle line necessarily involves variation in strip speed to permit the tacking together of the ends of coils and of course there are unexpected mechanical delays which accompany any continuous operation. It was thus found to be necessary to provide phosphate coating solutions which would function to produce the necessary quantity of phosphate coating in a short time, e. g., less than 15 seconds, but which would nevertheless avoid the deposition of widely variant weight coatings even though a pickle line stoppage, measured in minutes, occurred.

The primary objective of this invention is to provide a process which enables the continuous coating of steel strip with a phosphate coating of sufficient uniformity in thickness to facilitate cold rolling, the uniformity enabling the holding of gauge during continuous cold rolling.

A further object of this invention is to provide a process for treating ferrous strip stock continuously in a pickle line which produces a phosphate coating which aids in the subsequent cold rolling and which leaves on the surface a sufficient quantity of phosphate residue to prevent

sticking when the cold rolled strip is annealed either in stacked sheet or coil form.

Another important objective of this invention is to provide phosphate coating solutions capable of producing on a continuously moving ferrous strip a coating of the necessary weight or thickness and of sufficient uniformity to permit the attainment of the desired gauge tolerance in conventional cold rolling.

Another object of this invention is to provide a process for continuously forming a corrosion-resistant phosphate coating on the surface of ferrous strip subsequent to an acid pickle which enables the elimination of the application of an oil coating after acid pickling and prior to cold rolling, which heretofore has been conventional in this art.

Still another object of this invention is to provide a process for continuously applying a phosphate coating to a ferrous strip moving through a pickle line which is of sufficient uniformity to facilitate subsequent continuous cold rolling while maintaining the desired gauge tolerance and which reduces the power required to effect a predetermined amount of reduction; to provide such a phosphate coating as to enable the cold rolling of ferrous sheet of unusual flatness.

Another object is to provide such a phosphate coating to enable the elimination of the use of a roughened surface roll such as a Pangborn roll in a reversing mill or in the last stand of a multiple stand mill and yet produce a cold rolled sheet of suitable surface condition to present sticking on annealing.

Yet another object is to provide such a phosphate coating as to enable the annealing of sheets of such cold rolled strip in stacks up to 100% higher than heretofore used practice and at temperatures up to about 1750° F.; to provide such a phosphate coating as to enable the subsequent stamping, in the hardened cold rolled condition of various parts such as electric motor laminations, which after assembly may be annealed without sticking at temperatures as high as about 1750° F.

In accordance with the present invention it has been found that the above objectives may be realized if certain phosphate coating solutions are used under relatively closely controlled conditions in operation. It has been found that certain other phosphate coating solutions are either of minor benefit or are unsatisfactory for the purposes of this invention. Broadly stated the method of this invention comprises the steps of removing scale and corrosion products from the surface of ferrous strip stock, contacting the cleaned and continuously moving surface of the strip with an aqueous acidic zinc phosphate coating solution comprising as the essential coating producing ingredients in weight percent, 0.18 to 0.9 zinc, 0.5 to 2.0 PO_4 , 0.7 to about 2.5 ClO_3 and having a total acid of 10–60 points, and thereafter cold rolling the coated strip. Somewhat more desirable results are obtained if the solutions include as optional ingredients 0.1 to 2.4 NO_3 and 0.17 to 0.75% calcium by weight. By total acid of 10–60 points is meant that a 10 ml. sample of the solution requires 10–60 ml. of one-tenth normal sodium hydroxide to reach a phenolphthalein endpoint. It is satisfactory to employ a solution as above defined but containing the proportions of zinc and NO_3 which would result from adding zinc nitrate to the solution to reach the maximum total acid of 60 points so long as the ratio of calcium to zinc is maintained in the range of 0.4:1 to 1.1:1.

When the above proportions of constituents and the stated acidity range are maintained and the cleaned strip is passed through the solution, maintained at an elevated temperature of about 150° F. to 185° F., a substantially uniform coating is produced which is satisfactory for the purposes of this invention. "Substantially uniform" as used in this specification and in the appended claims is intended to mean that the coating is distributed over the entire surface of the strip such that the variation in the coating weight does not exceed 200 mg./sq. ft. from the

average coating weight which is prevalent on the strip. When the coating is substantially uniform, the actual weight of the coating which is required to facilitate the rolling operation may satisfactorily vary between a minimum of 50 mg./sq. ft. and a maximum of 1000 mg./sq. ft. Preferably the average coating weight, is maintained in the range of 150 to 400 mg./sq. ft. Coating weights lower than about 50 mg./sq. ft. have not been found to materially improve the rolling characteristics and after rolling do not leave a sufficient quantity of phosphate residue to prevent sticking on annealing, whereas coating weights above about 1000 mg./sq. ft., even though substantially uniform, make it difficult to maintain the desired gauge upon rolling. When the coating is substantially uniform and in the preferred weight range, the coated strip may be rolled in a series of passes to reduce the thickness to one-sixth the original thickness and yet sufficient phosphate residue remains after rolling to prevent sticking when sheets stacked fifty inches high are annealed at temperatures as high as about 1400° F. It has been observed that the presence of the residual phosphate on the surface after continuous cold rolling permits annealing at 100° F.–200° F. higher than temperatures heretofore utilizable so long as the pressure on the adjacent surfaces is comparable.

Due to the above referred to uncontrollable and unexpected stoppages which occur in the pickle line during normal operation, the relative proportions of ingredients in the above solutions have been found to be critical. When the proportions fall outside the limits given, the variation in coating weight which is obtained is so great that on subsequent rolling, difficulty is experienced in maintaining the desired gauge tolerance, or side slipping, ripping or tearing of the strip is encountered.

The best over-all results have been obtained from the use of solutions containing calcium. When calcium is present the ratio of calcium to zinc in the solution should be maintained within the range of 0.4 to 1 up to 1.1 to 1. Moreover, in these calcium-containing solutions, while it is possible to use ClO_3 concentrations as low as 0.15% it is desirable to maintain the chlorate concentration above about .3% and preferably between 0.4–0.6. The calcium containing solutions appear to produce a finer grain coating and this coating provides the maximum aid during rolling while concurrently producing the best surface finish.

After the coated strip emerges from the phosphate coating solution, it may, optionally, be rinsed in a conventional dilute aqueous solution of chromic acid or the equivalent. It is then recoiled on a receiving mandrel in a conventional manner. Rolling may then be effected on a reversing or multiple stand mill by employing the conventionally used lubricants during the rolling operation. Any of a number of satisfactory lubricants may be employed including oils, such as mineral oil, palm oil, rape seed oil, etc. Lubricants for this purpose are preferably used in aqueous form, either as a solution or emulsion. Dilute aqueous solutions consisting of, for example, 1% to 3% oil and the balance water, of a water soluble mineral oil, or a lard base oil together with an emulsifying agent, have been satisfactorily employed. One specific aqueous base lubricant which has been used with unusual success is a mixture of lard oil and a fatty acid and has the following analysis: Fatty acid (calculated as oleic acid), 12.9% by weight, iodine number 36.9 and a saponification number of 32.4. A small amount of an emulsifying agent to make this mixed oil water soluble is added to a solution containing 1%–2% of this mixed oil, balance water.

Hot rolled strip may be satisfactorily pickled in a pickling line consisting only of an aqueous sulfuric acid solution followed by a water rinse. Conventional acid pickling solutions, rinsing procedures and the like may be employed but it is desirable to process the hot rolled strip through an acidic pickling solution prior to its in-

5

roduction into the above disclosed phosphate coating solutions. It is important to avoid the contamination of the phosphate coating solution by the pickling acids and is therefore desirable to thoroughly rinse the strip emerging from the sulfuric acid pickle before its introduction into the phosphate coating solution. Where heavy mill scale is present on the hot rolled strip or other strip to be phosphate coated, conventional mechanical abrading means or molten alkali baths may be employed, prior to the acid pickling.

One unexpected advantage which accrues from the practice of the method of this invention is that it is unnecessary to employ shot blasted or roughened rolls in a reversing type mill to attain a surface finish that will not stick during coil or stack annealing. It is also unnecessary to employ a similar roll as the last position roll in a multiple stand mill.

The invention is illustrated in greater detail in the examples given below. It is to be understood that the examples given are intended to illustrate operative conditions only and are not intended to limit the invention to the specific proportions of ingredients set forth since the critical limits thereof have been hereinbefore.

Example I

An aqueous acidic phosphate solution tank was installed as the last station in a sulfuric acid pickling line comprising a sulfuric acid pickling station, a water rinse and the phosphate coating solution station. An aqueous acidic zinc phosphate solution was prepared in the phosphate station and analyzed to contain in percent w./v.: chlorate—0.17, nitrate—1.7, zinc—0.5, PO_4 —1.3, calcium—0.5; the bath operated at a total acid of 25–30 points and a free acid of 4–5. The bath was maintained at a temperature of about 150° F.–180° F. and hot rolled low carbon steel strip was fed through the sulfuric acid pickle, water rinsed and through the above solution at the rate of about 100 to 120 feet per minute which provided a contact time in the coating solution of about 10–12 seconds. This processing was continued for about 8 weeks during which time about 22,500,000 square feet of steel strip was processed through the solution. The coating weights obtained during this period had average weights between about 110 to 120 mg./sq. ft. with variations therefrom ranging from about 50 mg./sq. ft. to about 200 mg./sq. ft. The strip emerging from the phosphate coating solution was coiled in conventional manner. In some cases the coils were immediately rolled and in others a time delay of one or more days occurred before the rolling was done. Most of this treated strip stock was rolled under conditions which reduced the initial thickness from 0.1" to 0.068" in one pass, to 0.05" in two passes, to 0.038" in three passes, to 0.029" in four passes and 0.025" in five passes. The strip was rolled on a Bliss rolling machine of the reversing type and during the rolling there was a continuous flooding of the rolls and the work with an aqueous base lubricant. During this period of operation there were shutdowns in the pickle line travel for periods exceeding ten minutes and yet the variation in coating weight was insufficient to prevent the coil from being continuously cold rolled. Some of the coated stock was stamped directly into small horsepower motor laminations in the cold rolled hardened condition and it was observed that there was less wear on the dies when the stamping was done in the cold rolled hardened condition than otherwise. Other portions of this rolled strip were annealed in air and deoxidizing atmosphere furnaces in coils and in stacked sheet form at temperatures ranging from 1200° F. to as high as 1650° F. without encountering sticking between successive layers of the coil or between the sheets. Some of these stacks were increased to as high as 60 inches, from the normal 36" height and annealed at 1275° F. without sticking.

During the operation of the above solution, sodium

6

chlorate was added to raise the chlorate content to 0.32. The coating resulting from this solution was uniform in appearance and appeared to increase in weight less on line stoppage than solutions containing the lower chlorate percentages. Additional chlorate was added to raise the concentration to 0.38% and an even greater uniformity in the appearance of the coating was observed. On rolling the sheet coming from this bath, it was observed that less amperage was required on the Bliss rolling machine to effect the stepwise reduction in thickness than in any other conditions encountered, and 20%–30% less than the power required to roll uncoated strip stock. One of the most desirable bath compositions for the purposes of this invention is in percent w./v.: chlorate—0.36, nitrate—1.84, zinc—0.56, PO_4 —1.0, calcium—0.48, total acid—13.3.

Example II

Another solution, which does not contain calcium, which was found to be satisfactory was prepared in the phosphate coating station and analyzed to contain in percent w./v.: chlorate—0.43%, zinc—0.7%, PO_4 —1.1%, total acid 26.2%. Low carbon hot rolled strip operating in the same line as that described in Example I was processed through the bath of the above composition at a temperature of about 160° F.–170° F. until approximately 370,000 square feet of surface had passed through the bath. The coatings obtained in a contact time in the bath of 10–12 seconds were observed to be of conventional gray appearance and uniformly distributed over the surface. Typical coating weights obtained were about 188–205 mg./sq. ft. With chlorate concentration above 0.7% a substantially uniform coating was obtained even though the line stopped for times measured in minutes.

The coated strip was rolled while an aqueous base lubricant was flowing over the surface of the rolls and the strip. No trouble was encountered during the rolling, and the rolled strip upon examination revealed a uniformly flat surface having a smooth surface finish and a clean metallic appearance.

Example III

Another satisfactory bath was prepared and analyzed to contain in percent w./v.: chlorate—0.46, zinc—0.7, PO_4 —1.1, nitrate—0.27, total acid—28.2. With this solution maintained at a temperature of 160° F.–170° F. low carbon hot rolled strip passing through the same line as that described in Example I was processed through the bath until approximately 700,000 square feet of strip has been processed through the bath. Coating weights which resulted from this treatment varied from 264–370 mg./sq. ft. During the operation of this bath the chlorate content of the solution was increased in steps to .6%, .7% and gradually to 2%. As the proportion of chlorate exceeded 0.7% it was noted that line shutdowns had less effect on the increase in the resulting coating weight. The resulting coils were rolled in accordance with the procedure stated in Example I and satisfactory rolling conditions were obtained with the resulting rolled strip having uniformly smooth surface, being flat and having the appearance of clean metal.

Example IV

An aqueous acidic zinc solution was prepared, placed in the phosphate coating station and analyzed to contain in percent w./v.: zinc—0.55, PO_4 —0.82, NO_3 1.17. Sodium nitrite was added to the solution to produce a concentration of 0.0005% and maintained at or above that concentration during use. The bath had a total acid of 20 points. The bath was maintained at a temperature of 180° F.–185° F. and hot rolled low carbon steel strip was processed through the bath in the line and under similar conditions described in Example I. When the coil was moving through the bath at the regular speed of 100–120 feet/minute, the coating weights

obtained varied from about 150–200 mg./sq. ft. When the pickle line was stopped for a period of ten minutes the coating weight on the strip which was emerged in the tank during this stoppage was in the range of 800–1000 mg./sq. ft. Upon rolling this coil it was found that this heavy phosphate coating weight area caused slipping and tearing of the strip as it passed through the rolls.

What is claimed is:

1. A method for treating ferrous strip which comprises the steps of pickling the strip, contacting the cleaned strip while the same is moving with an aqueous acidic zinc phosphate solution comprising as the essential coating producing ingredients in weight percent, 0.18–0.9 zinc, 0.5–2.0 PO_4 and 0.7–2.5 ClO_3 , said solution having a total acid in the range of 10–60 points, maintaining said strip in contact with said solution until a phosphate coating is formed on the surface of said strip, said coating having a weight in the range of about 50 mg./per sq. ft. to about 1000 mg./per sq. ft. and varying from the average coating weight prevalent on said strip by not more than about 200 mg./per sq. ft., and thereafter continuously cold rolling the said strip.

2. A method for treating ferrous strip which comprises the steps of pickling the strip, contacting the cleaned strip while the same is moving with an aqueous acidic zinc phosphate solution comprising as the essential coating producing ingredients in weight percent, 0.18–0.9 zinc, 0.5–2.0 PO_4 , 0.15–2.5 ClO_3 , 0.1–2.4 NO_3 , 0.17–0.75 calcium, said solution having a total acid in the range of 10–60 points, controlling the temperature so as to produce a coating having a weight in the range of 50–1000 mg./per sq. ft. and varying from the average weight prevalent on said strip by not more than about 200 mg./per sq. ft., and thereafter continuously cold rolling the said strip.

3. A method for treating ferrous strip which comprises the steps of pickling the strip, contacting the cleaned strip while the same is moving with an aqueous acidic zinc phosphate solution comprising as the essential coating producing ingredients in weight percent, 0.18–0.9 zinc, 0.5–2.0 PO_4 , 0.15–2.5 ClO_3 , 0.1–2.4 NO_3 , 0.17–0.75 calcium, said solution having a total acid in the range of 10–60 points, controlling the temperature so as to produce a coating having a weight in the range of 50–1000 mg./per sq. ft. and varying from the average coating weight prevalent on said strip by not more than about 200 mg./per sq. ft., rinsing said coating strip in a dilute aqueous chromic acid solution and thereafter cold rolling said strip.

4. A method in accordance with claim 2 wherein said chlorate is present in a concentration between 0.3 and 0.6%.

5. A method in accordance with claim 1 wherein the

continuous rolling is performed while continuously flooding said strip with an aqueous base lubricant.

6. A method in accordance with claim 2 wherein said rolling is performed while said strip is continuously flooded with a dilute aqueous lubricant consisting essentially of 97%–99% water and 1–3% of a mixture of fatty acid and an emulsifying agent, said fatty acid containing the equivalent of 12.9% by weight of oleic acid, having an iodine number of 36.9 and a saponification number of 32.4.

7. A method in accordance with claim 2 wherein said coating has a weight in the range of about 150–400 mg./per sq. ft.

8. A method in accordance with claim 2 wherein the ratio of calcium to zinc in the solution is within the range of 0.4–1 and 1.1–1.

9. A ferrous strip which may readily be continuously cold rolled and which has an acidic phosphate coating thereon, said coating having a weight in the range of about 50 mg./per sq. ft. to about 1000 mg./per sq. ft. and varying from the average coating weight prevalent on said strip by not more than about 200 mg./per sq. ft., said strip having been pickled and then contacted with an aqueous acidic zinc phosphate solution comprising as the essential coating producing ingredient in weight percent, 0.18%–0.9% zinc, 0.5%–2% PO_4 and 0.7%–2.5% ClO_3 , said solution having a total acid in the range of 10–60 points.

10. A cold rolled ferrous strip having a residual acid phosphate coating thereon produced by contacting said strip, prior to the cold rolling thereof and subsequent to a pickling thereof, with an aqueous acidic zinc phosphate solution comprising as the essential coating producing ingredients in weight percent, 0.18–0.9 zinc, 0.5–2.0 PO_4 and 0.7–2.5 ClO_3 , 0.1–2.4 NO_3 , 0.17–0.75 calcium, said solution having a total acid in the range of 10–60 points, said phosphate coating having a weight in the range of about 50 mg./per sq. ft. to about 1000 mg./per sq. ft. and varying the average coating weight prevalent on said strip by not more than about 200 mg./per sq. ft.

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