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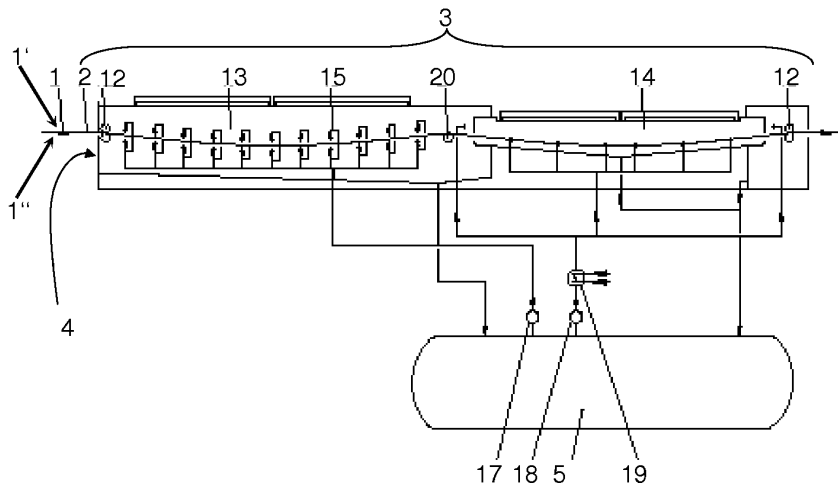
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(54) **Method of treating a steel strip, especially for a pickling treatment of the steel strip and system for treating a steel strip**

(57) The present invention relates to method for treating a steel strip by means of a treatment liquid in a treatment station, the treatment station comprising at least a spray section, an immersion section, and a common collection means for the treatment liquid, wherein the steel strip comprises carbon steel and is a continuous steel strip being oriented substantially horizontally, both in its longitudinal and transverse directions, wherein the steel strip has a top surface and a bottom surface, wherein the method comprises transporting the steel strip continuously through the treatment station in a transport direction, the transport direction being parallel to the longitudinal direction of the steel strip, such that

-- in a first step, the treatment liquid is sprayed onto the top surface of the steel strip and onto the bottom surface of the steel strip while the steel strip being in the spray section of the treatment station,  
-- in a second step, the steel strip is immersed in the treatment liquid while the steel strip being in the immersion section of the treatment station, wherein, while treating the steel strip, the treatment liquid is continuously pumped out of the common collection means and through both the spray section and the immersion section of the treatment station, wherein spraying of the treatment liquid onto the top and bottom surfaces of the steel strip is provided using spray nozzles.

FIG. 2



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## Description

### BACKGROUND

**[0001]** The present invention relates to a method for treating a steel strip, especially for a pickling treatment of the steel strip, by means of a treatment liquid in a treatment station, the treatment station comprising a treatment tank.

**[0002]** Furthermore, the present invention relates to a system for treating a steel strip, especially for a pickling treatment of the steel strip, by means of a treatment liquid in a treatment station, the treatment station comprising a treatment tank.

**[0003]** The steel strip to be treated according to the method of the present invention and in a system of the present invention is a carbon steel.

**[0004]** In pickling processes, metal surfaces are treated by removing impurities such as typically rust or scale using treatment liquids, or pickle liquors, typically containing strong acids.

**[0005]** These impurities may occur during metal forming processes, in particular rolling and/or heat treatment. During the hot rolling process of metal strips a scale layer, mainly consisting of different metal oxides, is formed. The scale layer needs to be removed before further processing the steel strip. This is typically done in an acid pickling process, wherein the scale layer is dissolved in the acid, followed by a rinsing section to completely remove the pickling solution. So-called "secondary scale" is formed as the steel strip passes continuously through the hot strip finishing line and over the roller table where it cools and to some extent also in the coiling machine, where the strip is wound up into coils. Depending on the grade of material, on the final thickness of the hot-rolled strip, and on the rolling speed, both the thickness of the scale and its chemical composition can vary.

**[0006]** Scale itself is chemically quite similar to rust, being made up of iron and oxygen bonded together in various molecular arrangements. Like rust, scale typically develops at the surface of the steel product where the metal surface is exposed to air.

**[0007]** To eliminate this scale, the most common approach today is to use a pickling line having one or a plurality of acid baths, typically using a plurality of pickling tanks or pickling stations in a row, normally containing hydrochloric acid at a certain temperature in the range of typically between 50 °C and 95 °C. Cumulatively or alternatively other strong acids are used to descale or clean the metal surfaces, e.g. hydrochloric acid, sulfuric acid, etc. may be used as pickling agents (or treatment liquid) for pickling of e.g. ferrous metals.

**[0008]** The steel strip is pulled (or pushed or both pulled and pushed) through the pickling line - especially the treatment tank (or pickling tank) - at a certain speed (e.g. up to a couple of meters per second), then rinsed - typically with water -, and dried, normally air-dried. During pulling and/or pushing of the steel strip through the pick-

ling line the layer of scale dissolves in the acid.

**[0009]** The concentration of the acid itself becomes depleted during the pickling operation, so that it is necessary to add fresh acid continuously. However, large amounts of spent acids are not only hazardous to the environment but usually also expensive. Thus it is desirable to reduce the amount of required acid for a given metal surface to be treated or to regenerate the spent acids for reuse. Furthermore, the pickling operation should be carried out such that the regeneration of the acids spent can be realized in a comparatively simple and comparatively environmentally compatible manner.

**[0010]** Since the beginning of pickling in general and strip pickling in particular developments in this field had the target to improve the efficiency with regards to pickling time, consumption of chemicals and energy, and surface quality. In the beginning, pickling lines were operated with H<sub>2</sub>SO<sub>4</sub>. Later HCl replaced H<sub>2</sub>SO<sub>4</sub> due to shorter pickling time, lower consumption and the possibility of total regeneration of the acid. Pickling acids are consumed during the pickling process. The acid dissolves the oxide scale and metal salts are formed. H<sub>2</sub>SO<sub>4</sub> mainly forms FeSO<sub>4</sub> which can be removed from the pickling liquid and has to be disposed and consequently has to be replaced by fresh H<sub>2</sub>SO<sub>4</sub>. HCl on the contrary forms mainly FeCl<sub>2</sub> and a minor amount of FeCl<sub>3</sub> during the pickling process. Both can be converted back to HCL in the so called pyrohydrolysis reaction using fluidized bed or spray roaster regeneration plants resulting in a complete recovery of the spent pickling acid. Another advantage of HCl as pickling liquid is the fact that HCl acts less aggressive to the base metal than H<sub>2</sub>SO<sub>4</sub> and consequently reducing the risk of over-pickling.

**[0011]** Beside the type of acid which is used during the pickling process, other factors influence the pickling efficiency. Higher temperature of the pickling acid for example reduces the required time which is needed to completely remove the scale layer. Therefore modern strip pickling lines using HCl as pickling liquid are operated at temperatures ranging from about 80 °C to about 90 °C. Since the pickling in acid containing pickling solutions is a chemical or electrochemical process, the media and energy exchange between the pickling acid and the strip surface is highly important with regards to the pickling efficiency.

**[0012]** Today pickling lines are designed as shallow tank turbulence installations comprising of several consecutive pickling tanks. The steel strip is pulled or pushed through the treatment tanks. The complete pickling section is arranged as a cascade, i.e. the fresh or regenerated acid is added to the last treatment tank (i.e. the most downstream treatment tank according to the direction of movement of the steel strip) and is then processed in a countercurrent flow to the strip transport direction in order to maximize the use of the pickling acid. At the entry and exit of the treatment tanks, wringer rolls are installed to remove the pickling acid from the strip to the greatest possible extent in order to enhance the cascade effect.

German patent disclosure DE 40 31 234 describes this technology.

**[0013]** Inside the treatment tank, the pickling acid is injected on both sides of the tank creating a high turbulence between the strip surface and the pickling acid.

**[0014]** The pickling acid is then overflowing from the treatment tank to a circulation tank from where it is again injected into the treatment tank by means of pumps. The high turbulence reduces the thickness of the liquid boundary layer on the strip surface resulting in an improved media and energy exchange and consequently reducing the required pickling time.

**[0015]** Another well-known pickling method is the spray pickling, wherein the pickling acid is directly sprayed onto the strip surface using several spray nozzles installed both above and below the steel strip, cf. e.g. document DE 42 28 808 A1. The pickling acid is then collected in a circulation tank from where it is pumped to the spray nozzles and sprayed on to the strip surface again. The spray nozzles are typically operated at a pressure above 1 bar. Due to the high impulse of the pickling acid sprayed onto the strip surface, the pickling efficiency and consequently the pickling time can be further improved. However this technology has never been used commercially in strip pickling lines. Laboratory tests, carried out for different steel grades, have proven, in particular when using HCl containing pickling solution, that the pickling speed of spray-pickling is up to five times higher compared to the shallow tank turbulence technology. However the dissolving speed of the base metal is increased in the same way or even further. Therefore, the pickling process is difficult to control with a high risk of over pickling the metal strip. One of the reasons for this aggressiveness with regards to the base metal is the formation of  $\text{FeCl}_3$  in the pickling acid. The spray nozzles used in the spray pickling technology create fine droplets with a high surface which are in direct contact with air. The air, in particular the oxygen contained in the air, dissolves in the pickling acid and oxidizes the  $\text{FeCl}_2$  together with the HCl forming  $\text{FeCl}_3$ . While HCl is a non oxidizing acid and therefore dissolving the base metal only slowly,  $\text{FeCl}_3$  is an oxidizing agent, consequently increasing the dissolving speed of the base material. In a pure spray pickling process the  $\text{FeCl}_3$  concentration can reach 60 g/l and above.

Another drawback of the increased  $\text{FeCl}_3$  concentration in the pickling acid is the effect on the regeneration process of the spent pickling acid. Spent pickling acid is typically regenerated using the pyrohydrolysis process. In this process  $\text{FeCl}_2$  and  $\text{FeCl}_3$  are converted back to HCl and  $\text{Fe}_2\text{O}_3$ .  $\text{FeCl}_3$  however has a much lower evaporation temperature than  $\text{FeCl}_2$  and evaporates in the pyrohydrolysis reactor causing very fine  $\text{Fe}_2\text{O}_3$  particles below 1  $\mu\text{m}$  in size when converted to  $\text{Fe}_2\text{O}_3$ . These fine particles are difficult to remove from the process off-gases causing high dust emissions.

## SUMMARY

**[0016]** It is therefore an object of the present invention to provide method and a system for an improved steel strip treatment, especially pickling, such that fixed investment as well as maintenance costs are reduced, the treatment and pickling process is realized comparatively quickly, with high quality, and in an environmentally friendly manner.

**[0017]** The object of the present invention is achieved by a method for treating a steel strip, especially for a pickling treatment of the steel strip, by means of a treatment liquid in a treatment station, the treatment station comprising a treatment tank with a spray section and an immersion section, and the treatment station comprising a common collection means for the treatment liquid, wherein the steel strip comprises carbon steel and is a continuous steel strip being oriented substantially horizontally, both in its longitudinal and transverse directions, wherein the steel strip has a top surface and a bottom surface, wherein the method comprises transporting the steel strip continuously through the treatment station in a transport direction, the transport direction being parallel to the longitudinal direction of the steel strip, such that

-- in a first step, the treatment liquid is sprayed onto the top surface of the steel strip and onto the bottom surface of the steel strip while the steel strip being in the spray section of the treatment station,  
 -- in a second step, the steel strip is immersed in the treatment liquid while the steel strip being in the immersion section of the treatment station,

wherein, while treating the steel strip, the treatment liquid is continuously pumped out of the common collection means and through both the spray section and the immersion section of the treatment station, wherein spraying of the treatment liquid onto the top and bottom surfaces of the steel strip is provided using spray nozzles.

**[0018]** According to the present invention, it is thereby advantageously possible to provide a treatment station that requires comparatively low installation costs as well as reduced maintenance costs. The present invention is related to a process for chemical or electrochemical treatment of the surface of carbon steel, preferably strip shaped, wherein the material is treated with a pickling solution, preferably containing HCl, in one or more treatment tanks to remove an oxide scale layer which was previously formed during the hot rolling process of the metal strip (steel strip). This treatment is needed to reach a clean surface for either further processing it in a cold rolling process or for direct commercial use.

**[0019]** According to the present invention, it is preferred that the process for chemical or electrochemical treatment of the surface of carbon steel is conducted using a pickling solution containing HCl as the only pickling agent, wherein the advantages of spray pickling are used

to a maximum extend. Furthermore the process shall be controllable minimizing the risk of over-pickling so that the process can be realized in commercially used industrial scale pickling lines.

**[0020]** According to the present invention, the spent acid of such a process is of a quality such that it can be treated in regeneration plants without additional investment considering in particular the  $\text{FeCl}_3$  concentration in such spent acid.

**[0021]** The present invention is also directed to the possibility to revamp existing pickling lines, in particular the treatment tanks, and to use more efficient pickling technology with improved efficiency while re-using existing equipment in order to reduce installation costs, as for example acid circulation circuits etc. can be reused.

**[0022]** According to the present invention, it is advantageously possible that such requirements can be achieved by the present invention, comprising a pickling process using an HCl containing pickling solution as the only pickling acid, wherein the material to be treated (i.e. the steel strip) is processed horizontally through one or more treatment tanks which are - in case of more than one treatment tank - operated as a pickling cascade.

**[0023]** According to the present invention, each single treatment tank (of the treatment station) of the above described process comprises of one spray pickling zone and one dip pickling zone arranged as one unit using one common circulation circuit, i.e. one common circulation tank (common collection means) with several pump circuits as required. All pickling acid coming from the dip section and the spray section are collected and mixed in the common circulation tank (common collection means) and pumped back to the above mentioned two pickling sections (of the treatment tank of the treatment station). Inside the single pickling tank (treatment tank), a guide roll underneath the strip located between the spray and pickling section might be required to better position the steel strip inside the treatment tank. Typically, a wringer roll unit - as it is typically installed between two pickling sections - is not required. Preferably the first section of the treatment tank is a spray section while the second section of the dip pickling type, preferably with high efficiency such as shallow tank turbulence technology.

**[0024]** According to the present invention, the steel strip is treated - in the treatment tank of the treatment station - by means of a treatment liquid such that the same treatment liquid is used both in the spray section and in the immersion section of the treatment tank. Advantageously, it is thereby possible to realize the treatment station (having both the spray section and the immersion section) in a more cost effective manner as the same common collection means (as well as at least a part of the circulation system) can be used for both the spray section and the immersion section, hence reducing the costs for realizing the possibility to treat the steel strip by means of both the spray section and the immersion section.

**[0025]** According to the present invention, the steel

strip comprises carbon steel and is a continuous steel strip being oriented substantially horizontally, both in its longitudinal and transverse directions, at least at the treatment station. This means that steel strip is mostly horizontally oriented in its transverse direction but is allowed to be sagging in its longitudinal direction. The height variation through the treatment station of the steel strip in its longitudinal direction may reach, e.g., up to 0,5 m. Preferably, also between the treatment station or between the plurality of treatment stations, the height variations of the steel strip in its longitudinal direction are also comprised up to 0,5 m. Generally, it is preferred according to the present invention that the height variation of the steel strip in its longitudinal direction is comprised between up to 0,5 m throughout the complete treatment system, that potentially (and typically) comprises a plurality of treatment stations one after the other in the transport direction of the steel strip.

**[0026]** According to the present invention, the treatment liquid is sprayed - in a first step and by means of nozzles - onto the top surface of the steel strip and onto the bottom surface of the steel strip while the steel strip is in the spray section of the treatment station. In second step (that is not necessarily subsequent to the first step but could also be preceding the first step), the steel strip is immersed in the treatment liquid while the steel strip is in the immersion section of the treatment station. For the treatment of the steel strip, the treatment liquid of the treatment station is continuously pumped out of the common collection means (of that treatment station) and through both the spray section and the immersion section of the treatment tank, wherein spraying of the treatment liquid onto the top and bottom surfaces of the steel strip is provided using spray nozzles.

**[0027]** According to the present invention, two pickling technologies are directly combined in one treatment tank (i.e. in one treatment station), i.e. using physically the same pickling acids (or the same treatment liquid) in both pickling sections (i.e. in both the spray section and the immersion section of the considered treatment station), as described. By doing so, the concentration of  $\text{FeCl}_3$  can be kept below a critical level throughout the entire pickling process, guaranteeing a uniform pickling result without the risk of over-pickling. Furthermore the spent acid of such process can be easily regenerated in regeneration plants without additional investment to reach the legally required emission values, especially regarding dust emissions.

**[0028]** According to the present invention, the efficiency of the treatment process (or pickling process) is increased. Tests have proven that a certain increase in the  $\text{FeCl}_3$  concentration reduces the pickling time also for the dip pickling process. Consequently the process according to the present invention uses the advantage of the high efficient spray pickling process while the efficiency of the dip pickling process is improved as well, due to the common use of the pickling acid (i.e. the same treatment liquid is used both in the spray section and the

immersion section of one and the same treatment station), and the consequently increased  $\text{FeCl}_3$  level. Of course, in (the typical) case that more than one treatment stations are used in a pickling line or steel strip pickling installation, this does not mean that the same treatment liquid is used in all of such different treatment stations. To the contrary, in case of a plurality of treatment stations (i.e. having each a treatment tank comprising a spray section and an immersion section), a different treatment liquid is normally used for a different treatment station; however within the same treatment station/treatment tank, the same treatment liquid is used for both kinds of pickling processes (spray and dip pickling). Thereby, it is advantageously possible that the drawbacks of a comparatively high concentration in  $\text{FeCl}_3$  can be avoided that would typically arise in case of combining spray pickling and dip pickling using different treatment liquids in the same treatment station.

**[0029]** According to the present invention, the design of the treatment line or pickling line is done in such a way that it is advantageously possible that the treatment stations or treatment tanks can easily replace existing treatment tanks in case of a required revamp (or refurbishment) while the circulation circuits can be reused. This is mainly attributed to the fact that the spray pickling technology and the dip pickling technology (i.e. the spray section and the immersion section) are combined in one treatment tank (i.e. as part of one treatment tank).

**[0030]** The design of the present invention also allows the possibility to operate the treatment tanks without an additional (external) circulation tank - or common collection means - (i.e. external or separate to the treatment tank). In such an embodiment, the treatment tank itself, in particular the area underneath the spray section, and, if required, also underneath the dip section, is used as circulation tank (or common collection means), i.e. the circulation tank (or common collection means) is realized in a manner integrated with the treatment tank. This is advantageous for the replacement (refurbishment) of deep bath treatment tanks which have often been operated without circulation circuits. In this case only the pump circuit needs to be added while the circulation tank is incorporated (or integrated) in the treatment tank.

**[0031]** According to a preferred embodiment of the present invention, the spray section comprises an effective spray length in parallel to the longitudinal direction of the steel strip such that - during the first step - the top and bottom surfaces of the steel strip receive the treatment liquid while being located within the effective spray length, wherein the immersion section comprises an effective immersion length in parallel to the longitudinal direction of the steel strip such that - during the second step - the steel strip is immersed - with its top and bottom surfaces - in the treatment liquid while being located within the effective immersion length, wherein the effective spray length and the effective immersion length are provided having a ratio of between and including 30:70 to 70:30, especially a ratio of 50:50.

**[0032]** According to the present invention, it is thereby advantageously possible to flexibly adapt process parameters of a pickling line to fit best with the intended operative use after construction. By means of defining the length of the immersion section (at a given transport speed of the steel strip through the pickling line), the time is defined during which the treatment liquid is effectively treating the steel strip in the immersion section. By means of defining the length of the spray section (equally at a given transport speed of the steel strip through the pickling line), the maximum time of spray pickling is defined in relation to the dip pickling time.

**[0033]** According to another preferred embodiment of the present invention, the effective spray length and hence the ratio of the effective spray length vs. the effective immersion length is varied by activating only a part of the spray nozzles.

**[0034]** According to the present invention, it is thereby advantageously possible to vary the spray pickling time even during operational use of the pickling line, i.e. by de-activating a part of the spray nozzles. By selectively activating and/or de-activating groups of spray nozzles, it is advantageously possible according to the present invention, that also the manner or the intensity of the spray pickling step can be varied in operational use of the pickling line, e.g. by using only every second spray nozzle such that spray pickling is less intensive in the spray section.

**[0035]** According to a preferred embodiment of the present invention, the spray section is located - along the transport direction of the steel strip - upstream with respect to the immersion section. According to an alternative preferred embodiment of the present invention, the spray section is located - along the transport direction of the steel strip - downstream with respect to the immersion section.

**[0036]** According to the present invention, it is thereby advantageously possible to provide the possibility of different pickling line architectures. E.g., it is advantageously possible (in case that at least two treatment stations are used) to provide both treatment stations such that the spray section is located upstream with respect to the immersion section (i.e. the steel strip passes the spray section first and afterwards the immersion section): This results in a pickling sequence of the kind of a spray and dip pickling (using a first treatment liquid) in the first (or upstream) treatment station, followed by a spray and dip pickling (using a second treatment liquid) in the second (or downstream) treatment station. Alternatively, it is also advantageously possible (in case that at least two treatment stations are used) to provide the first treatment station such that the spray section is located downstream with respect to the immersion section (i.e. the steel strip passes the immersion section first and afterwards the spray section), and to provide the second treatment station such that the spray section is located upstream with respect to the immersion section (i.e. the steel strip passes the spray section (of the second treatment station)

first and afterwards the dip section (of the second treatment station)): This results in a pickling sequence of the kind of a dip and spray pickling (using a first treatment liquid) in the first (or upstream) treatment station, followed by a spray and dip pickling (using a second treatment liquid) in the second (or downstream) treatment station. Of course, these building blocks of two treatment stations can be either repeated or combined with other treatment stations or configurations of treatment stations.

**[0037]** According to a preferred embodiment of the present invention, the method comprises using - besides using the treatment liquid in the treatment station - a further treatment liquid in a further treatment station, the further treatment station comprising a further treatment tank with a further spray section and a further immersion section, and the further treatment station comprising a further common collection means for the further treatment liquid, wherein the method comprises transporting the steel strip continuously through the further treatment station in the transport direction such that

-- in a third step, the further treatment liquid is sprayed onto the top surface of the steel strip and onto the bottom surface of the steel strip while the steel strip being in the further spray section of the further treatment station,

-- in a fourth step, the steel strip is immersed in the further treatment liquid while the steel strip being in the further immersion section of the further treatment station,

wherein, while treating the steel strip, the further treatment liquid is continuously pumped out of the further common collection means and through both the further spray section and the further immersion section of the further treatment station, wherein spraying of the further treatment liquid onto the top and bottom surfaces of the steel strip is provided using further spray nozzles, wherein the third and fourth steps are preceding the first and second steps or are subsequent to the first and second steps.

**[0038]** According to the present invention, it is thereby advantageously possible to combine at least two inventive treatment stations in a pickling line. Of course, it is also possible and preferred according to the present invention to combine such two inventive treatment stations with a conventional treatment station (i.e. having solely a spray section or solely an immersion section in a treatment tank) or with a plurality of conventional treatment stations. In such an architecture of the pickling line, the two inventive treatment station are either located directly subsequent one after the other along the transport direction of the steel strip or the combination with one or a plurality of conventional treatment stations is provided such that the treatment station (or the first treatment station) is located upstream according to the transport direction of the steel strip with respect to a conventional treatment station (or with respect to a plurality of conven-

tional treatment stations) and downstream with respect to this or these conventional treatment station(s) is located the further treatment station (or second treatment station) according to the present invention.

**[0039]** According to another preferred embodiment of the present invention, the treatment liquid and/or the further treatment liquid comprises

-- hydrochloric acid in a concentration ranging from and including 150 g/l to and including 250 g/l and  
 -- FeCl<sub>3</sub> in a concentration ranging from and including 10 g/l to and including 35 g/l, especially in a concentration ranging from and including 15 g/l to and including 30 g/l or especially in a concentration ranging from and including 19 g/l to and including 26 g/l and,

-- FeCl<sub>2</sub><sup>+</sup> ions in a concentration ranging from and including 30 g/l to and including 300 g/l, especially in a concentration ranging from and including 30 g/l to and including 60 g/l or in a concentration ranging from and including 130 g/l to and including 180 g/l or in a concentration ranging from and including 230 g/l to and including 300 g/l.

**[0040]** According to the present invention, it is thereby advantageously possible to combine a high efficiency of the pickling process while retaining the possibility to comparatively easily regenerated the used pickling acids (treatment liquids).

**[0041]** The present invention also relates to a system for treating a steel strip, especially for a pickling treatment of the steel strip, by means of a treatment liquid in a treatment station, the system comprising the treatment station, wherein the treatment station comprises a treatment tank with a spray section, an immersion section, and the treatment station comprising a common collection means for the treatment liquid,

wherein the steel strip comprises carbon steel and is a continuous steel strip being oriented substantially horizontally, both in its longitudinal and transverse directions, wherein the steel strip has a top surface and a bottom surface,

wherein the system is configured to transport the steel strip continuously through the treatment station in a transport direction, the transport direction being parallel to the longitudinal direction of the steel strip, such that

-- the treatment liquid is sprayed onto the top surface of the steel strip and onto the bottom surface of the steel strip while the steel strip being in the spray section of the treatment station,

-- the steel strip is immersed in the treatment liquid while the steel strip being in the immersion section of the treatment station,

wherein the system is configured such that the treatment liquid is continuously pumped out of the common collection means and through both the spray section and the

immersion section of the treatment station, wherein the system comprises spray nozzles such that the treatment liquid is sprayed onto the top and bottom surfaces of the steel strip using the spray nozzles.

**[0042]** According to the present invention, it is thereby advantageously possible to provide a system (or a treatment station) that requires comparatively low installation costs as well as reduced maintenance costs. According to the present invention, it is advantageously possible to combine the advantages of spray pickling and dip pickling and to minimize the risk of over-pickling. It is furthermore advantageous that the spent acid of such a system is of a quality such that it can be treated in regeneration plants without additional investment considering in particular the  $\text{FeCl}_3$  concentration in such spent acid.

**[0043]** According to a preferred embodiment of the present invention - especially regarding the inventive system -, the spray section comprises an effective spray length in parallel to the longitudinal direction of the steel strip such that the top and bottom surfaces of the steel strip receive the treatment liquid while being located within the effective spray length, wherein the immersion section comprises an effective immersion length in parallel to the longitudinal direction of the steel strip such that the steel strip is immersed - with its top and bottom surfaces - in the treatment liquid while being located within the effective immersion length, wherein the effective spray length and the effective immersion length are provided having a ratio of between and including 30:70 to 70:30, especially a ratio of 50:50.

**[0044]** According to the present invention, it is thereby advantageously possible to flexibly adapt process parameters of a pickling line to fit best with the intended operative use after construction.

**[0045]** According to a preferred embodiment of the present invention - especially regarding the inventive system -, the spray section is located - along the transport direction of the steel strip - upstream with respect to the immersion section. According to an alternative preferred embodiment of the present invention - especially regarding the inventive system -, the spray section is located - along the transport direction of the steel strip - downstream with respect to the immersion section.

**[0046]** According to the present invention, it is thereby advantageously possible to flexibly adapt process parameters of a pickling line to fit best with the intended operative use after construction.

**[0047]** According to a preferred embodiment of the present invention - especially regarding the inventive system -, the common collection means for the treatment liquid of both the spray section and the immersion section is a collection means separated from the treatment tank of the treatment station.

**[0048]** According to the present invention, it is thereby advantageously possible to build the treatment tank in a very cost effective manner such that especially the volume of the treatment tank is comparably small (and hence less treatment liquid is to be used). The treatment

liquid is pumped through the common collection means (or circulation tank) that is separated from the treatment tank.

**[0049]** According to a preferred embodiment of the present invention - especially regarding the inventive system -, the common collection means for the treatment liquid of both the spray section and the immersion section is a collection means integrated with the treatment tank of the treatment station, especially integrated such that the bottom part of the treatment tank forms the common collection means.

**[0050]** According to the present invention, it is thereby advantageously possible to realize the treatment station in a very cost effective manner as no separate common collection means (or circulation tank) is required.

**[0051]** According to another preferred embodiment of the present invention - related to both the method and the system -, the length of the treatment station is preferably 20 m or less, preferably between 16 m and 20 m. The treatment station comprising both the spray section and the immersion section is preferably assembled using two main components of the treatment tank such that the treatment tank is - after assembling the two main components - integrally formed using the two main components.

**[0052]** According to the present invention, it is thereby advantageously possible to provide the two main components forming the treatment tank such that each of the main components have a maximum length of 11,6 m, i.e. the two main components have a length of 11, 6 m or less. Thereby, it is advantageously possible to transport these main components of the treatment tank, used in a treatment station according to the inventive method, such that no welding of the two main components is required. Preferably, the main components of the treatment tank are slid into one another. This enables a much faster setup of the treatment station which is especially advantageous in case of re-furbishing existing pickling lines, as the down-time due to the refurbishment can be considerably reduced. According to the present invention, it is preferred that one of the main components of the treatment tank realizes the spray section of the treatment station and the other of the main components of the treatment tank realizes the immersion section of the treatment station.

**[0053]** According to a preferred embodiment of the present invention - especially regarding the inventive system -, the system comprises - besides the treatment liquid in the treatment station - a further treatment liquid in a further treatment station, the further treatment station comprising a further treatment tank with a further spray section and a further immersion section, and the further treatment station comprising a further common collection means for the further treatment liquid, wherein the system is configured such that the steel strip is transported continuously through the further treatment station in the transport direction such that

-- the further treatment liquid is sprayed onto the top surface of the steel strip and onto the bottom surface of the steel strip while the steel strip being in the further spray section of the further treatment station,  
 -- the steel strip is immersed in the further treatment liquid while the steel strip being in the further immersion section of the further treatment station,

wherein the system is configured such that the further treatment liquid is continuously pumped out of the further common collection means and through both the further spray section and the further immersion section of the further treatment station, wherein the system comprises further spray nozzles such that the further treatment liquid is sprayed onto the top and bottom surfaces of the steel strip using the further spray nozzles.

**[0054]** According to the present invention, it is thereby advantageously possible to combine at least two inventive treatment stations in a pickling line. Of course, it is also possible and preferred according to the present invention to combine such two inventive treatment stations with a conventional treatment station (i.e. having solely a spray section or solely an immersion section in a treatment tank) or with a plurality of conventional treatment stations.

**[0055]** According to a preferred embodiment of the present invention, the system comprises - besides the treatment liquid in the treatment station and the further treatment liquid in the further treatment station - a third treatment liquid in a third treatment station, the third treatment station comprising a third treatment tank with a third spray section and a third immersion section, and the third treatment station comprising a third common collection means for the third treatment liquid.

**[0056]** According to the present invention, it is thereby advantageously possible to combine at least three inventive treatment stations in a pickling line. Of course, it is also possible and preferred according to the present invention to combine such three inventive treatment stations with a conventional treatment station (i.e. having solely a spray section or solely an immersion section in a treatment tank) or with a plurality of conventional treatment stations.

**[0057]** According to a further preferred embodiment of the present invention, the system comprises - besides the treatment liquid in the treatment station, the further treatment liquid in the further treatment station, and the third treatment liquid in the third treatment station - a fourth treatment liquid in a fourth treatment station, the fourth treatment station comprising a fourth treatment tank with a fourth spray section and a fourth immersion section, and the fourth treatment station comprising a fourth common collection means for the fourth treatment liquid. According to other embodiments, also the combination of five treatment stations according to the present invention is possible and preferred according to the present invention.

**[0058]** According to another preferred embodiment of

the present invention, the treatment liquid and/or the further treatment liquid and/or the third treatment liquid comprises

5 -- hydrochloric acid in a concentration ranging from and including 150 g/l to and including 250 g/l and  
 -- FeCl<sub>3</sub> in a concentration ranging from and including 10 g/l to and including 35 g/l, especially in a concentration ranging from and including 15 g/l to and including 30 g/l or especially in a concentration ranging from and including 19 g/l to and including 26 g/l and,  
 -- FeCl<sub>2</sub> in a concentration ranging from and including 30 g/l to and including 300 g/l, especially in a concentration ranging from and including 30 g/l to and including 60 g/l or in a concentration ranging from and including 130 g/l to and including 180 g/l or in a concentration ranging from and including 230 g/l to and including 300 g/l.

**[0059]** According to the present invention, it is thereby advantageously possible to combine a high efficiency of the pickling process while retaining the possibility to comparatively easily regenerated the used pickling acids (treatment liquids).

**[0060]** These and other characteristics, features and advantages of the present invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention. The description is given for the sake of example only, without limiting the scope of the invention. The reference figures quoted below refer to the attached drawings.

## 35 BRIEF DESCRIPTION OF THE DRAWINGS

### **[0061]**

**Figure 1** schematically illustrates a treatment system comprising three different treatment stations, each one being configured according to the present invention, i.e. having a treatment tank with both a spray section and an immersion section such that a common collection means and the same treatment liquid is used for the treatment of the steel strip in both the respective spray section and the immersion section.

**Figure 2** schematically illustrates a first embodiment of a treatment station having a treatment tank and a common collection means separated from the treatment tank, the treatment tank having its spray section and its immersion section to treat the steel strip with a common treatment liquid circulating between - and within - the common collection means on the one hand, and the spray and immersion sections on the other hand.

**Figure 3** schematically illustrates a second embodiment of a treatment station having a treatment tank and a common collection means separated from the treatment tank, the treatment tank having its spray section and its immersion section to treat the steel strip with a common treatment liquid circulating between - and within - the common collection means on the one hand, and the spray and immersion sections on the other hand.

#### DETAILED DESCRIPTION

**[0062]** The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. The drawings described are only schematic and are non-limiting. In the drawings, the size of some of the elements may be exaggerated and not drawn on scale for illustrative purposes.

**[0063]** Where an indefinite or definite article is used when referring to a singular noun, e.g. "a", "an", "the", this includes a plural of that noun unless something else is specifically stated.

**[0064]** Furthermore, the terms first, second, third and the like in the description and in the claims are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described of illustrated herein.

**[0065]** Figure 1 schematically illustrates a treatment system comprising three different treatment stations 3, 31, 32 as an example of a pickling line according to the present invention. In one possible and preferred implementation of the pickling line for the treatment of a steel strip 1, represented in Figure 1, all three treatment stations 3, 31, 32 represent treatment stations according to the present invention, i.e. having a treatment tank with both a spray section and an immersion section such that a common collection means and the same treatment liquid is used for the treatment of the steel strip in both the respective spray section and the immersion section. In this implementation or architecture of the pickling line, all three treatment stations 3, 31, 32 are realized either according to a first embodiment of the present invention, represented in Figure 2 for the exemplary case of the treatment station being represented by reference sign 3, or according to a second embodiment of the present invention, represented in Figure 3 for the exemplary case of the treatment station being represented by reference sign 3. Alternatively, a part of the three treatment stations 3, 31, 32 is or are realized according to the first embodiment of the present invention (Figure 2) and another part is or are realized according to the second embodiment of the present invention (Figure 3). In the context of the present invention, the terms 'treatment station' and 'first

treatment station' as well as 'further treatment station' and 'second treatment station' are used synonymously and only aim to differentiate the treatment stations from one another. Typically, the naming convention typically (but not necessarily) relates to the location of a treatment station along the transport direction of the steel strip, the transport direction being represented by reference sign 2. In the implementation represented in Figure 1, a treatment station (or first treatment station) 3 is located upstream of a further treatment station (or second treatment station) 31. The further treatment station (or second treatment station) 31 is located upstream of a third treatment station 32. The treatment station (or first treatment station) 3 comprises a treatment tank (or first treatment tank) 4, and a common collection means (or first common collection means) 5. The further treatment station (or second treatment station) 31 comprises a further treatment tank (or second treatment tank) 41, and a further common collection means (or second common collection means) 51. The third treatment station 32 comprises a third treatment tank 42, and a third common collection means 52. In the exemplary implementation of the pickling line represented in Figure 1 (where all treatment stations are configured according to the present invention), all three treatment stations 3, 31, 32 each have a spray section and an immersion section as part of their respective treatment tank 4, 41, 42, i.e. the treatment station (or first treatment station) 3 has a spray section (or first spray section) and an immersion section (or first immersion section) using a treatment liquid (or first treatment liquid), the further treatment station (or second treatment station) 31 has a further spray section (or second spray section) (not depicted in Figure 1) and a further immersion section (or second immersion section) (not depicted in Figure 1) using a further treatment liquid (or second treatment liquid), and the third treatment station 32 has a third spray section (not depicted in Figure 1) and a third immersion section (not depicted in Figure 1) using a third treatment liquid. For the exemplary case of the treatment station 3 (first treatment station 3), a first and a second embodiment of the present invention is schematically shown in Figures 2 and 3.

**[0066]** Figure 2 schematically illustrates the first embodiment of the treatment station 3 having the treatment tank 4 and the common collection means 5 separated from the treatment tank 4, the treatment tank 4 having its spray section 13 and its immersion section 14 to treat the steel strip 1 with a common treatment liquid circulating between - and within - the common collection means 5 on the one hand, and the spray and immersion sections 13, 14 on the other hand.

**[0067]** Figure 3 schematically illustrates a second embodiment of a treatment station 3 having the treatment tank 4 and the common collection means 5 separated from the treatment tank 4, the treatment tank 4 having its spray section 13 and its immersion section 14 to treat the steel strip 1 with a common treatment liquid circulating between - and within - the common collection means 5

on the one hand, and the spray and immersion sections 13 on the other hand.

**[0068]** Figures 1, 2 and 3 combined illustrate the inventive treatment process and system (or treatment station) for chemical or electrochemical treatment of the surface of the steel strip 1, the steel strip 1 being a carbon steel strip. The steel strip 1 is first horizontally transported through the treatment stations 3, 31, 32 in which the steel strip 1 is treated with a treatment liquid in the form of a pickling acid, normally containing HCl. At least one of the treatment stations 3, 31, 32 (or their respective treatment tanks 4, 41, 42) comprises a spray pickling section (as represented in Figures 2 and 3 as spray section 13 of the treatment station 3) and a dip pickling section (as represented in Figures 2 and 3 as immersion section 14 of the treatment station 3) according to the present invention. Figure 1 shows an exemplary implementation with three treatment stations 3, 31, 32 (each having a treatment tank) as a preferred embodiment, however the number of treatment stations (and treatment tanks) is at least one and is not limited to three.

**[0069]** All treatment stations 3, 31, 32 comprise a common collection means, respectively (i.e. the respective treatment tanks 4, 41, 42 are connected to respective common collection means (or circulation tanks) 5, 51, 52), wherein the common collection means 5, 51, 52 are either (i.e. potentially for each treatment station 3, 31, 32 differently) realized as separate tanks as shown in the first embodiment represented in Figure 2 or are realized as common collection means 5, 51, 52 integrated in the respective treatment tank 4, 41, 42 as shown in Figure 3.

**[0070]** In the exemplary embodiment shown in Figure 1, the common collection means (or circulation tanks) 5, 51, 52 are operated as a cascade, i.e. the fresh or regenerated acid (i.e. the treatment liquid) is added (cf. reference sign 54) to the last common collection means (or last circulation tank) 52 - i.e. being related to the most downstream treatment station 32 according to the transport direction 2 of the steel strip 1 - and is consequently transferred to the other common collection means (or circulation tanks) in counter direction to the strip transport direction 2. Thereby, the level of free acid is the highest in the third treatment liquid (circulating in the third treatment station 32), the level of free acid is medium in the further treatment liquid (second treatment liquid) (circulating in the further (second) treatment station 31), and lowest in the treatment liquid (first treatment liquid) (circulating in the (first) treatment station 3. Finally the spent acid is removed (reference sign 55) from the (first) common collection means (or (first) circulation tank) 5. After the pickling treatment in the three treatment stations 3, 31, 32 (in the exemplary implementation shown in Figure 1), the steel strip 1 is further processed in section 6 which comprises a rinse section and a dryer, if required.

**[0071]** According to the first embodiment of the common collection means (or circulation tank) 5, shown in Figure 2, the treatment station 3 comprises the treatment tank 4 with a separate common collection means 5 (or

separate circulation tank 5). At the entry and exit section, wringer rolls 12 are installed to remove pickling acid from the strip and to guide the steel strip 1 inside the treatment tank 4. The wringer roll 12 in the entry section is only used when the treatment tank is the first tank in the pickling process like the treatment station 3 in Figure 1. The following treatment stations (or treatment tanks), like treatment stations 31, 32 in Figure 1, do not need such wringer roll 12. In the exemplary representation of Figure 2 (i.e. not necessarily), the first part (according to the transport direction of the steel strip 1) of the treatment tank 4 is a spray pickling section 13 or spray section 13, followed by a dip pickling section 14 or immersion section 14. In the spray pickling section 13, spray nozzles 15 are mounted above and below the surface of the steel strip 1. The pickling acid (or treatment liquid) is pumped from the circulation tank 5 (or common collection means 5) by means of pumps 17, 18 to both the spray pickling section 13 and the dip pickling section 14. In one or more of the pump circuits, a heat exchanger 19 is installed to heat the pickling acid (treatment liquid) to the required temperature. If required, a guide roll 20 can be installed between the spray pickling section 13 and the dip pickling section 14 in order to reduce the slack of the strip.

**[0072]** According to the second embodiment of the common collection means (or circulation tank) 5, shown in Figure 3, the treatment station 3 comprises the treatment tank 4 with an integrated common collection means 5. The other components of the treatment station 3 are analogous to the description of Figure 2.

**[0073]** While specific embodiments of the invention have been shown and described in detail to illustrate the inventive principles, it will be understood that the invention may be embodied otherwise without departing from such principles.

**[0074]** For example, the pickling line is configured for a maximum width of the steel strip 1 of 1890 mm, a maximum speed of the steel strip 1 of 255 m/min. Furthermore exemplarily, the distance of the spray nozzles 15 to the steel strip 1 (both from the spray nozzles to the top surface 1' of the steel strip 1, and to the bottom surface 1" of the steel strip 1) is 200 mm or approximately 200 mm. Additionally, the distance of the spray nozzles 15 to each other in the lateral direction of the steel strip 1 corresponds to 200 mm or approximately 200 mm. Additionally, the distance of the spray nozzles 15 to each other in the longitudinal direction of the steel strip 1 corresponds to 500 mm or approximately 500 mm. The treatment liquid is preferably pumped out of the spray nozzles having a pressure of between and including 1 bar to and including 3 bar, and the amount of treatment liquid per spray nozzle is preferably 12 l/min or approximately 12 l/min. For example, the total number of spray nozzles per treatment station corresponds to 306 or approximately 306, and the amount of pumped treatment liquid per treatment station corresponds to 220 m<sup>3</sup>/h or approximately 220 m<sup>3</sup>/h.

**[0075]** Test trials were carried out in a pilot plant. The

pilot plant consisted of two treatment stations (each having a treatment tank) both arranged as described in the present invention with a first spray pickling section followed by a dip pickling section in each of the treatment tanks. The treatment tanks were designed so that the length of both sections was approximately the same. The pickling acid used was HCl with a concentration of approx. 200 g/l total acid in both tanks. The material treated during the test runs were different IF steel grades (interstitial Free steel), which belong to the group of steel grades that are more difficult to pickle mainly due to their high recoiling temperature. The test results have proven that the pickling time could be reduced by 40 - 45% compared to the conventional pickling process using dip pickling with shallow tank turbulence technology, while the FeCl<sub>3</sub> concentration was constantly below 30 g/l which is considered to be uncritical as far as the acid regeneration process is concerned. All tested materials showed uniform pickling results without any signs of over-pickling.

**[0076]** In another test using the same pilot plant, the material was treated with a reduced temperature of the pickling acid (treatment liquid). The results showed that the temperature could be reduced from 90°C down to 70 °C while still reaching the same pickling time as for the conventional dip pickling process with shallow tank turbulence technology. This result is equivalent to a 20 % reduction of the energy which is needed to keep the process temperature in the pickling process.

**[0077]** As an example of the operation of the system and especially of the use of the treatment liquids as a cascade, an example is given of the concentration values for an example of using three treatment stations in a pickling line:

In the first treatment station 3, the concentration of HCl is in the range of between and comprising 205 g/l to and comprising 220 g/l, the concentration of FeCl<sub>2</sub> is in the range of between and comprising 260 g/l to and comprising 278 g/l, the concentration of FeCl<sub>3</sub> is in the range of between and comprising 22 g/l to and comprising 26 g/l. The temperature of the treatment liquid is in the range of between and comprising 88 °C to and comprising 91 °C.

In the second treatment station 31, the concentration of HCl is in the range of between and comprising 201 g/l to and comprising 211 g/l, the concentration of FeCl<sub>2</sub> is in the range of between and comprising 140 g/l to and comprising 146 g/l, the concentration of FeCl<sub>3</sub> is in the range of between and comprising 21 g/l to and comprising 26 g/l. The temperature of the treatment liquid is in the range of between and comprising 88 °C to and comprising 91 °C.

In the third treatment station, the concentration of HCl is in the range of between and comprising 193 g/l to and comprising 206 g/l, the concentration of FeCl<sub>2</sub> is in the range of between and comprising 43 g/l to and comprising 47 g/l, the concentration of FeCl<sub>3</sub> is in the range of between and comprising 19

g/l to and comprising 22 g/l. The temperature of the treatment liquid is in the range of between and comprising 88 °C to and comprising 91 °C.

## 5 REFERENCE SIGNS

### [0078]

1	steel strip
10 2	transport direction of the steel strip
3	treatment station
4	treatment tank (of the treatment station)
5	common collection means (of the treatment station)
15 12	wringer roll(s)
13	spray section (of the treatment station)
14	immersion section (of the treatment station)
15	spray nozzles (of the treatment station)
17, 18	pumps
20 19	heat exchanger
20	guide roll(s)
31	further treatment station
41	further treatment tank (of the further treatment station)
25 51	further common collection means (of the further treatment station)
32	third treatment station
42	third treatment tank (of the third treatment station)
30 52	third common collection means (of the third treatment station)
54	feeding of fresh treatment liquid
55	removing of used treatment liquid

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## Claims

1. Method for treating a steel strip (1), especially for a pickling treatment of the steel strip (1), by means of a treatment liquid in a treatment station (3), the treatment station (3) comprising a treatment tank (4) with a spray section (13) and an immersion section (14), and the treatment station (3) comprising a common collection means (16) for the treatment liquid, wherein the steel strip (1) comprises carbon steel and is a continuous steel strip (1) being oriented substantially horizontally, both in its longitudinal and transverse directions, wherein the steel strip (1) has a top surface (1') and a bottom surface (1''), wherein the method comprises transporting the steel strip (1) continuously through the treatment station (3) in a transport direction (2), the transport direction being parallel to the longitudinal direction of the steel strip (1), such that

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-- in a first step, the treatment liquid is sprayed onto the top surface (1') of the steel strip (1) and

onto the bottom surface (1 ") of the steel strip (1) while the steel strip (1) being in the spray section (13) of the treatment station (3),

-- in a second step, the steel strip (1) is immersed in the treatment liquid while the steel strip (1) being in the immersion section (14) of the treatment station (3),

wherein, while treating the steel strip (1), the treatment liquid is continuously pumped out of the common collection means (16) and through both the spray section (13) and the immersion section (14) of the treatment station (3), wherein spraying of the treatment liquid onto the top and bottom surfaces (1', 1 ") of the steel strip (1) is provided using spray nozzles (15).

2. Method according to claim 1, wherein the spray section (13) comprises an effective spray length in parallel to the longitudinal direction of the steel strip (1) such that - during the first step - the top and bottom surfaces (1', 1 ") of the steel strip (1) receive the treatment liquid while being located within the effective spray length, wherein the immersion section (14) comprises an effective immersion length in parallel to the longitudinal direction of the steel strip (1) such that - during the second step - the steel strip (1) is immersed - with its top and bottom surfaces (1', 1") - in the treatment liquid while being located within the effective immersion length, wherein the effective spray length and the effective immersion length are provided having a ratio of between and including 30:70 to 70:30, especially a ratio of 50:50.
3. Method according to one of the preceding claims, wherein the effective spray length and hence the ratio of the effective spray length vs. the effective immersion length is varied by activating only a part of the spray nozzles (15).
4. Method according to one of the preceding claims, wherein - along the transport direction of the steel strip (1) - the spray section (14) is located upstream or downstream with respect to the immersion section (15).
5. Method according to one of the preceding claims, wherein the method comprises using - besides using the treatment liquid in the treatment station (3) - a further treatment liquid in a further treatment station (31), the further treatment station (31) comprising a further treatment tank (41) with a further spray section and a further immersion section, and the further treatment station (31) comprising a further common collection means (51) for the further treatment liquid, wherein the method comprises transporting the steel strip (1) continuously through the further treatment station (31) in the transport direction such that

-- in a third step, the further treatment liquid is sprayed onto the top surface (1') of the steel strip (1) and onto the bottom surface (1 ") of the steel strip (1) while the steel strip (1) being in the further spray section of the further treatment station (31),

-- in a fourth step, the steel strip (1) is immersed in the further treatment liquid while the steel strip (1) being in the further immersion section of the further treatment station (31),

wherein, while treating the steel strip (1), the further treatment liquid is continuously pumped out of the further common collection means (51) and through both the further spray section and the further immersion section of the further treatment station (31), wherein spraying of the further treatment liquid onto the top and bottom surfaces (1', 1 ") of the steel strip (1) is provided using further spray nozzles, wherein the third and fourth steps are preceding the first and second steps or are subsequent to the first and second steps.

6. Method according to one of the preceding claims, wherein the treatment liquid and/or the further treatment liquid comprises
  - hydrochloric acid in a concentration ranging from and including 150 g/l to and including 250 g/l and
  - $\text{FeCl}_3$  in a concentration ranging from and including 10 g/l to and including 35 g/l, especially in a concentration ranging from and including 15 g/l to and including 30 g/l or especially in a concentration ranging from and including 19 g/l to and including 26 g/l and,
  - $\text{FeCl}_2$  in a concentration ranging from and including 30 g/l to and including 300 g/l, especially in a concentration ranging from and including 30 g/l to and including 60 g/l or in a concentration ranging from and including 130 g/l to and including 180 g/l or in a concentration ranging from and including 230 g/l to and including 300 g/l.
7. System for treating a steel strip (1), especially for a pickling treatment of the steel strip, by means of a treatment liquid in a treatment station (3), the system comprising the treatment station (3), wherein the treatment station (3) comprises a treatment tank (4) with a spray section (13), an immersion section (14), and the treatment station (3) comprising a common collection means (16) for the treatment liquid, wherein the steel strip (1) comprises carbon steel and is a continuous steel strip (1) being oriented substantially horizontally, both in its longitudinal and transverse directions, wherein the steel strip (1) has a top surface (1') and a bottom surface (1"), wherein the system is config-

ured to transport the steel strip (1) continuously through the treatment station (3) in a transport direction, the transport direction being parallel to the longitudinal direction of the steel strip (1), such that

- the treatment liquid is sprayed onto the top surface (1') of the steel strip (1) and onto the bottom surface (1'') of the steel strip (1) while the steel strip (1) being in the spray section (13) of the treatment station (3),
- the steel strip (1) is immersed in the treatment liquid while the steel strip (1) being in the immersion section (14) of the treatment station (3),

wherein the system is configured such that the treatment liquid is continuously pumped out of the common collection means (16) and through both the spray section (13) and the immersion section (14) of the treatment station (3), wherein the system comprises spray nozzles (15) such that the treatment liquid is sprayed onto the top and bottom surfaces (1', 1'') of the steel strip (1) using the spray nozzles (15).

8. System according to claim 7, wherein the spray section (13) comprises an effective spray length in parallel to the longitudinal direction of the steel strip (1) such that the top and bottom surfaces (1', 1'') of the steel strip (1) receive the treatment liquid while being located within the effective spray length, wherein the immersion section (14) comprises an effective immersion length in parallel to the longitudinal direction of the steel strip (1) such that the steel strip (1) is immersed - with its top and bottom surfaces (1', 1'') - in the treatment liquid while being located within the effective immersion length, wherein the effective spray length and the effective immersion length are provided having a ratio of between and including 30:70 to 70:30, especially a ratio of 50:50.
9. System according to one of claims 7 to 8, wherein - along the transport direction of the steel strip (1) - the spray section (14) is located upstream or downstream with respect to the immersion section (15).
10. System according to one of claims 7 to 9, wherein the common collection means (5) for the treatment liquid of both the spray section (13) and the immersion section (14) is a collection means (5) separated from the treatment tank (4) of the treatment station (3).
11. System according to one of claims 7 to 9, wherein the common collection means (5) for the treatment liquid of both the spray section (13) and the immersion section (14) is a collection means (5) integrated with the treatment tank (4) of the treatment station (3), especially integrated such that the bottom part

of the treatment tank (4) forms the common collection means (5).

12. System according to one of claims 7 to 11, wherein the system comprises - besides the treatment liquid in the treatment station (3) - a further treatment liquid in a further treatment station (31), the further treatment station (31) comprising a further treatment tank (41) with a further spray section and a further immersion section, and the further treatment station (31) comprising a further common collection means (51) for the further treatment liquid, wherein the system is configured such that the steel strip (1) is transported continuously through the further treatment station (31) in the transport direction such that

- the further treatment liquid is sprayed onto the top surface (1') of the steel strip (1) and onto the bottom surface (1'') of the steel strip (1) while the steel strip (1) being in the further spray section of the further treatment station (31),
- the steel strip (1) is immersed in the further treatment liquid while the steel strip (1) being in the further immersion section of the further treatment station (31),

wherein the system is configured such that the further treatment liquid is continuously pumped out of the further common collection means (51) and through both the further spray section and the further immersion section of the further treatment station (31), wherein the system comprises further spray nozzles such that the further treatment liquid is sprayed onto the top and bottom surfaces (1', 1'') of the steel strip (1) using the further spray nozzles.

13. System according to one of claims 7 to 12, wherein the system comprises - besides the treatment liquid in the treatment station (3) and the further treatment liquid in the further treatment station (31) - a third treatment liquid in a third treatment station (32), the third treatment station (32) comprising a third treatment tank (42) with a third spray section and a third immersion section, and the third treatment station (32) comprising a third common collection means (52) for the third treatment liquid.
14. System according to one of claims 7 to 13, wherein the treatment liquid and/or the further treatment liquid and/or the third treatment liquid comprises
  - hydrochloric acid in a concentration ranging from and including 150 g/l to and including 250 g/l and
  - FeCl<sub>3</sub> in a concentration ranging from and including 10 g/l to and including 35 g/l, especially in a concentration ranging from and including 15

g/l to and including 30 g/l or especially in a concentration ranging from and including 19 g/l to and including 26 g/l and,

-- FeCl<sub>2</sub> in a concentration ranging from and including 30 g/l to and including 300 g/l, especially in a concentration ranging from and including 30 g/l to and including 60 g/l or in a concentration ranging from and including 130 g/l to and including 180 g/l or in a concentration ranging from and including 230 g/l to and including 300 g/l.

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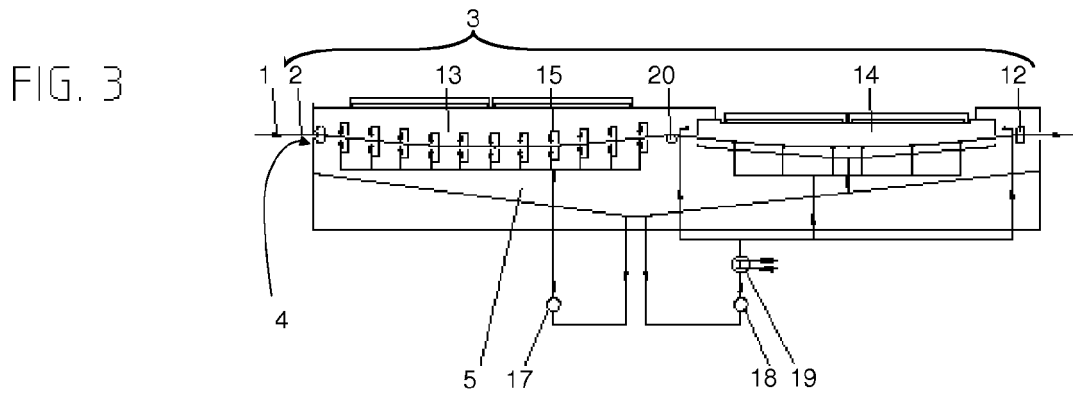
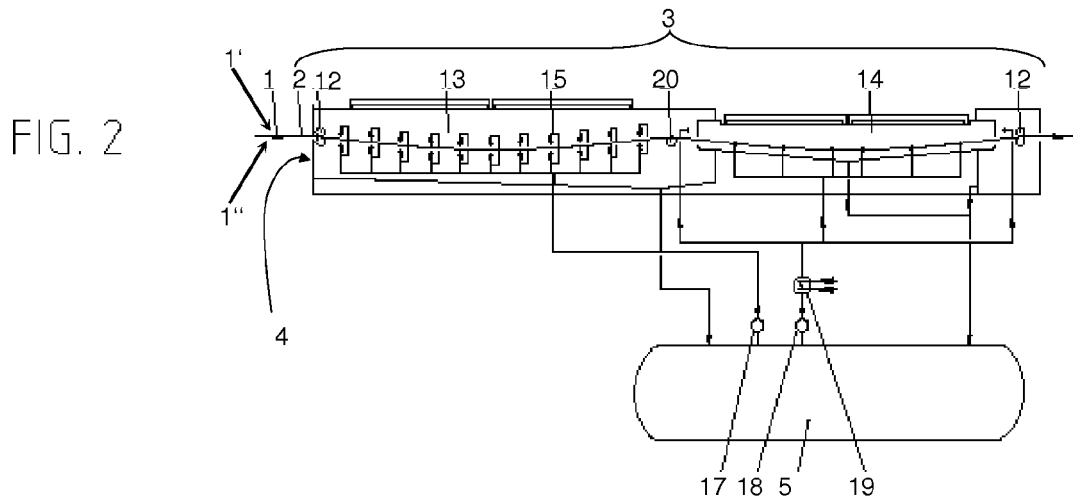
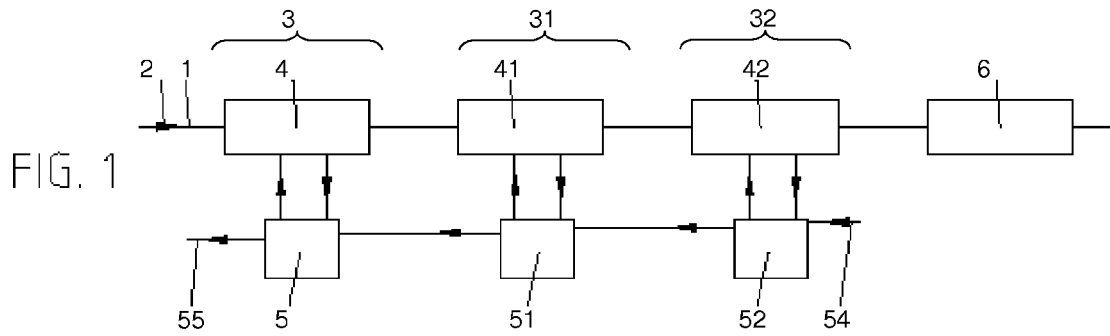
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EUROPEAN SEARCH REPORT

Application Number  
EP 14 19 5949

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X A	JP H06 128774 A (NIPPON STEEL CORP) 10 May 1994 (1994-05-10) * claims 1-2; figures 1-3 * -----	1-9, 11-14 10	INV. C21D8/02 C23G1/08
X A	WO 02/081776 A1 (AK PROPERTIES INC [US]) 17 October 2002 (2002-10-17) * claims 1-18; figures 1-3 * -----	1-9, 11-14 10	
A	US 5 759 307 A (BERGER HEINZ DIPL ING [DE] ET AL) 2 June 1998 (1998-06-02) * claims 1-18 *	1-14	
A	US 5 840 173 A (WALDMANN RALF [DE]) 24 November 1998 (1998-11-24) * claims 1-15 * -----	1-14	
			TECHNICAL FIELDS SEARCHED (IPC)
			C21D C23G
The present search report has been drawn up for all claims			
Place of search <b>Munich</b>		Date of completion of the search <b>11 May 2015</b>	Examiner <b>Liu, Yonghe</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

1  
EPO FORM 1503 03.02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 14 19 5949

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

11-05-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP H06128774 A	10-05-1994	NONE	
WO 02081776 A1	17-10-2002	AT 309397 T BR 0208748 A CA 2443687 A1 CN 1505697 A DE 60207225 D1 DE 60207225 T2 EP 1377692 A1 JP 4180925 B2 JP 2004525262 A KR 20030093306 A MX PA03009218 A US 2002179113 A1 WO 02081776 A1 ZA 200307744 A	15-11-2005 22-06-2004 17-10-2002 16-06-2004 15-12-2005 27-07-2006 07-01-2004 12-11-2008 19-08-2004 06-12-2003 07-03-2005 05-12-2002 17-10-2002 04-10-2004
US 5759307 A	02-06-1998	AT 235584 T DE 19532278 A1 EP 0770707 A1 ES 2196111 T3 JP H09125271 A US 5759307 A	15-04-2003 06-03-1997 02-05-1997 16-12-2003 13-05-1997 02-06-1998
US 5840173 A	24-11-1998	EP 0814180 A1 JP H1060697 A TW 382640 B US 5840173 A	29-12-1997 03-03-1998 21-02-2000 24-11-1998

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- DE 4031234 [0012]
- DE 4228808 A1 [0015]