

UNITED STATES PATENT OFFICE

2,162,846

PICKLING

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Serial No. 185,228

1 Claim. (Cl. 148—8)

This invention relates to the pickling of steel, and is particularly concerned with the pickling of steel to condition it for subsequent enameling.

In the production of enameled hollow ware, steel sheets are pressed into the desired forms, such as pots and pans, pickled in an acid solution to remove grease, scale or other contamination, rinsed to cleanse them of the acid and subsequently coated with a suitable vitreous material and fired to effect fusion of the latter. Ordinarily, the pickling bath is a water solution of sulphuric acid heated to a suitable temperature and sometimes containing various other compounds, such as hydrochloric acid as a pickling accelerator.

Enameled hollow ware, and in fact all enameled ware, is subject to fish-scaling. This term is common to the trade and is defined by the "Enameler's Dictionary", published by the Ferro Enamel Corporation, as being "a defect, sometimes occurring in sheet steel enamel ware where a small chip or particle of the fired coating literally jumps from the surface, the chips being half-moon shaped particles somewhat resembling the scales of a fish. Fish-scale is a ground coat defect but often does not occur until the cover coat has been applied and burned."

This definition may be amplified by saying that the defect is sometimes not evidenced until the product is in the customer's hands.

It is generally conceded that fish-scaling troubles may be traced to the pickling operation, the idea being that the pickling fails to effect complete cleansing, small localized unclean surfaces preventing the subsequent bonding of the enamel. Efforts to prevent the trouble have been made by increasing the temperature of the pickling bath, increasing the acid concentration of the bath, prolonging the pickling time, etc. Various other expedients have also been attempted. However, so far as is known, those skilled in the art have to date failed to provide a solution for completely remedying the evil under discussion, and it is an object of the present inventors to completely eliminate fish-scaling and, more broadly, to generally improve the pickling of steel, whether in the enameling industry or in other industries requiring the cleansing of steel.

With the foregoing in mind, the present invention includes the use of an acid pickling solution including at least .04 per cent. of hydrogen sulphide by volume. During pickling, suitable additions of hydrogen sulphide should be made to keep the hydrogen sulphide concentration at or above this value. The upper concentration limit

may be said to be only that beyond which blistering is encountered or practical difficulties occur by way of the hydrogen sulphide leaving the solution and becoming a nuisance. Blistering will not cause trouble up to a concentration of .10 per cent. by volume.

Since the invention was conceived primarily as an aid to the enameling industry, a specific example of the use of the above pickling solution will be disclosed in connection with the enameling of steel articles. Such a process includes immersing the steel articles to be enameled, and which must be cleaned, in an acid pickling solution having a hydrogen sulphide content constantly maintained at a concentration of at least .04 per cent. by volume of solution. The acid may be sulphuric acid, this being in most common use. The temperature of the bath should be sufficiently low that the maintenance of a hydrogen sulphide content of at least .04 per cent. by volume is practical. Although this may necessitate a lower pickling temperature than is usual, prolonged pickling does not thereby become a necessity because the hydrogen sulphide apparently functions as an accelerator. However, as will presently be found, the gas is not necessarily included primarily for this purpose.

After the articles are properly pickled they are removed from the solution in the usual manner. This means that they are not protected from the atmosphere but are carried in the pickling baskets from the pickling bath. The articles are then rinsed clean of the acid and, if necessary, subjected to the action of a suitable neutralizer. It will be found that the articles are conditioned, by the just described treatment, for application of the enameling material and for permanent bonding of the latter upon proper firing. Very little trouble from fish-scaling will be experienced and, in most instances, it will be found that fish-scaling is entirely absent.

Apparently the maintenance of the hydrogen sulphide content in the pickling solution at or above the described concentration produces the desired effect not only by acting as a pickling accelerator but also by functioning to prevent the permanent formation of water-insoluble iron compounds both in the pickling bath and while the articles are being carried to the water rinse. The ordinary sulphuric acid pickling bath, which remains on the articles while they are being carried through the air, is thought to result in the formation of insoluble iron compounds which subsequent water rinsing will not remove and

which, therefore, remain on the articles, thus preventing proper bonding of the enamel and ultimately causing fish-scaling troubles. The hydrogen sulphide prevents this action by reason of its strong reducing character, it functioning to either prevent the formation of insoluble iron compounds or, in case these compounds do form, to reduce them to water soluble compounds which may be easily removed. This protection exists both during pickling and during the transfer of the articles to the water rinse.

As hereinbefore intimated, the hydrogen sulphide content drops during pickling, it being necessary to introduce the gas from time to time to maintain the concentration described. Therefore, during the pickling process the solution should be analyzed from time to time and hydrogen sulphide added in quantities which the analyzation results indicate are necessary to maintain at least a .04 per cent. concentration by volume of hydrogen sulphide of the solution. The reason the hydrogen sulphide concentration is not given in weight percentage is because the specific gravity of pickling solutions increases during use, the proportioning of the gas by volume not being subject to this variable influence. Test volumes of the solution removed for testing purposes should be protected between the time of removal and the time of testing to prevent the

escape of hydrogen sulphide gas, since inaccurate results would otherwise be obtained.

In addition to introducing the hydrogen sulphide directly as a gas, lumps of iron-sulphide may be added to the pickling solution. The heavy lumps fall to the bottom where they are slowly dissolved by the acid, thereby liberating hydrogen sulphide gas continuously until exhausted. This method is believed most practical and economical and is therefore preferred. Sodium sulphide may be added, but since this compound is very light and reactive its effect is that of the sudden introduction of a large quantity of hydrogen sulphide rather than the continuing slow evolution resulting from the use of iron-sulphide. Sodium sulphide is, however, very useful in initially charging an acid pickling solution to the described concentration of hydrogen sulphide, iron sulphide being then used during pickling.

We claim:

A process of preparing steel articles for vitreous enameling, including immersing the articles in an acid pickling solution having a hydrogen sulphide content constantly maintained at a concentration of at least .04 per cent. by volume of the solution, removing the articles from said solution and rinsing them clean.

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