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EXAMINER

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CONDITIONING OF METAL SURFACES

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1 Claim. (Cl. 252—146)

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This invention relates to the conditioning of metal surfaces. Metallurgical operations involve various types of handling a metallic base. The preparation or cleaning desirably has to do with exposing uniformly the metal texture thruout. Expeditiously and reliably to achieve this end means that the stock is in most acceptable condition for direct use in its true state, as well as for receiving a coating, plating, or a wide range of surface applications thereto or thereon.

This invention has utility in accelerating bath treatment of the metal, say as ferrous sheets thru pickling for enameling thereof. The hindering factor, from normal exposure to the air or weathering conditions, is corrosion, or more seriously, scale. The problem to be solved has to do with the removal from the iron or steel, any and all objectionable substances or material thereon. This may arise from substances used in manufacture, such as oils, soaps and the like. More especilaly, the treatment is effective on scale, so snugly adhering from its oxidation bonding upon the metal. An acid pickling bath in which the materials are submerged, under an instance for use of the invention herein, has the attack materially expedited as well as effects advantages in a resulting superior product. This achievement is due to the introduction into the bath of an agent which, in itself, need not necessarily have traits to attack the iron or steel. The bath, into which the metal to be treated is immersed, serves as a menstruum or carrier. The fact that the invention treatment, with the substances or ingredients, brings about definite acceleration, establishes that the functioning of applicant's invention is contrary to any slowing down on the metal cleaning operation or reaction. Actually, the way is cleared for efficient pickling performance by the bath, with no detractive results from applicant's taking advantage of the liquid state of the bath to adapt it as a carrier for generally exposing the surface or surfaces open to pickling attack. At the surface or surfaces, the bath carrier for the relatively minimal quantity for the invention treatment agent is efficient in major scavenger-like performance.

Manufacturing processes have to do with various special handling operations. With metals, more particularly with iron and steel, there may be various heat treatments, annealing and forging. Various pickling baths are adapted to remove the oxide or scale. The baths, usually of acid, may predominantly be sulfuric acid, altho hydrochloric, hydrofluoric and nitric acids, as well as various combinations thereof, and even

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alkalis have place. Pickling baths of caustic soda and caustic potash have more value in the treatment of aluminum and magnesium articles. Phosphates are in other baths.

An instance under the invention herein may be taken of the treatment of sheet iron of say 20 gauge and of a character usually suitable for tin plating, galvanizing, electroplating or enameling. This sheet iron is submerged in a vat or tank of sulfuric acid of strength in the range of 7% acid by weight to 93% water. A course taken, to have the temperature somewhat above normal atmospheric, is helpful in establishing a reliable practice for holding to uniform operating conditions. While the operation may be acceptably carried thru at 150° F., or even lower, instances illustrative of performance efficiency herein have been taken at 160° F.

Sulfuric acid is adapted for its dissolving or penetrating action upon scales or oxide coatings. The acid eats its way thru the undesirable surface to the base, where the metal itself is more readily attacked. The sulfuric acid develops fissures or crack-like courses in the scale to reach the iron. The longer the interval of the bath, the deeper such eating is directly into the metal to etch it away. Hydrogen gas, generated by the chemical reaction of the sulfuric acid upon the iron, may be trapped under the scale surface about the crack or fissure to blast off scale particles. The seeming nature of this hydrogen is that it has responded to reaction and now has a trait of spreading out or locating as an inert film coating over the metal and the residual scale on the metal. The adsorbed film of gas is too thin to have buoyancy to rise as a bubble and thus to escape from the bath.

Applicant has realized that taking away of this deterrent hydrogen film by an oxygen agent may not be quite as promotive in clearing of oxide or permitting more rapid attack of the base metal, as may be desired, as proceeding therefrom along the periodic chart scale in the general sulfur, selenium, tellurium direction. Accordingly, the course adopted is to introduce a substance to react with this released hydrogen and get it away from the iron as a hydride, say as in hydrogen sulfide, hydrogen selenide, and hydrogen telluride.

In accordance with the practice of the invention, compounds may be taken which will produce finely divided sulfur in suspension, when added to an acid solution. A polysulfide, as well as micronized sulfur, selenium and tellurium, will answer. For a specific instance, sodium thiosulfate ($Na_2S_2O_3$) may be taken. Considering this salt as

carrying five molecules of water ($Na_2S_2O_3 \cdot 5H_2O$), and that but one of the sulfur atoms be released for the accelerating response herein, the proportion of this sodium thiosulfate may be one part in seven hundred by weight as to the weight of 7% sulfuric acid (H_2SO_4) in the bath, which would produce one part of reactive sulfur in five thousand, approximately, by weight as to the weight of the 7% sulfuric acid (H_2SO_4) in the bath.

In a ten minute interval, the attacking rate upon iron was speeded up from .07% to .19%. Increase in this nascent, colloidal-characteristic sulfur, in the experience hereunder, does not proportionally accelerate the pickling bath operation. Doubling, or for two parts of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in seven hundred, instead of one part as above, or two parts available of finely divided sulfur per five thousand parts sulfuric acid (H_2SO_4) in the 7% by weight acid bath, resulting from the breakdown of the two parts of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) per seven hundred parts sulfuric acid (H_2SO_4), seems to make no difference.

By the use of four parts in seven hundred, the attack rate is run up to the range of .3%, and when up to eight parts, the showing is only around .4%. This latter rate condition does not seem to be materially improved by further increase, even up to sixty-four parts in seven hundred of the sulfur carrying agent as to the acid. This prompts the applicant to reach the conclusion that an optimum condition is developed in the low proportion ranges as set forth.

Performance checkings with other substances of the periodic chart, more remote from oxygen than sulfur, seem to show about half the speed-up rate attributable to sulfur, when the metal acted upon approached cleanness at starting. However, when there was a heavy scale, and the treatment was continued thru to complete or full removal of such scale, then the results seem to bring the selenium and tellurium agents more closely to approximate that developed under like circumstances from sulfur treating agents.

Dispersion of the agent at the attack region upon the metal is effectively achieved in the form of fines, say of sulfur resulting from the addition of sodium polysulfide to an acid solution. These fines of sulfur provide a maximum of exposure area in the micron dimension range, and this seems to fit in very helpfully in working thru for the desired acceleration sought herein. The handling may be in batches, or thru continuous operation. The importance, in the latter instance, is quite noticeable in considering the material handled may have bath transit from 100' per minute set up to 300' per minute, and depending upon the physical dimensions of the solution tanks, acid concentration and temperature of the bath. The saving due to the acceleration may be not only in time, as in the continuous process, but in equipment, say as to bath dimension curtailment; in supplies, in reduced quantity of acid required, not offset by the relatively negligible quantity of accelerator of the general types herein disclosed, which may be selectively taken upon the conditions which, marketwise, seems more appropriate. A superior product with practical elimination of any objectionable etching is had under the accelerator treatment herein disclosed, as for the undesired coating removal, whether from iron, steel, alloys, copper, brass, zinc, or aluminum.

In pickling practice, the higher temperatures may increase the speed of reaction not quite one per cent per degree of temperature Fahrenheit rise, say from 150° F. to 170° F. Practically this discloses that by the use of applicant's invention there may be saving by less use of steam for heating the bath. When there be installed equipment and it is desired to have it conform to a materially increased production schedule, economically there may be hereunder a ready adaptation thereto.

Relatively to the chemically reactive bath, the ingredients disclosed herein for incorporation therewith are minimal in proportion. As a complementally reactive agent, say the dispersed nascent, crystalloidal or colloidal characteristic of micron fineness sulfur, possesses reactive properties of sufficient hydrogen pick-up efficiency to clear the surface being treated of the seemingly relatively inert hydrogen film. This film is so tenuously thin as not readily to gather into droplet masses, and thus, of itself, does not tend to rise in the solution to be clear of the metal. It is thus seen that the great surface area of the sulfur, as to its real mass or quantity, imparts under the treatment as herein disclosed, an efficient dispersion of reactant particles of penetratingly minute effectiveness to get to the film and form hydrogen sulfide. The dispersed sulfur is not of inhibitor-like retardant properties toward the active agent proper, say sulfuric acid of the solution. The functioning accordingly seems to be that the strength or reactive value of the bath more nearly approaches retention of its initial potency. The purpose of the treatment is to keep exposed the oxide or sulface portions to be removed. The course adopted hereunder is to eliminate the hydrogen film on said portions. The fines of the sulfur provide a maximum of area to react on the film. Generally the sulfuric acid is not spent in any way against the ingredient or ingredients introduced thru the accelerator treatment herein disclosed. Furthermore, hereunder, there be not occasion in any way to dissipate the pickling attack value of the sulfuric acid. The infinitesimal proportion relationship of the accelerator to the entire bath leaves the way open for the reactive agent and the accelerator each to pursue its reaction course, one not to the detriment of the other. In the more low ranges, the more wide seems to be the per-unit sulfur value.

The more heavy the scale, the longer the time interval which is normally required for complete removal, say in pickling of ferrous metal. Specifically in operating to such end, 7% H_2SO_4 solution has been operated to clear the metal of scale in 3½ min. Checking of this character of metal by the addition to the bath of accelerator, to the total weight of the acid, eight parts in seven hundred $Na_2S_2O_3$ shortened the operating time for complete de-scaling to 2½ min. There seems to be an attack factor relevant to the accelerator that it does not increase the mass of the material removed directly relatively to the acid, but as to the metal area or surface exposed. Even here it may show some buildup, but not directly in proportion to the acid attack total. Importance resides in the fact that it does not accelerate the root attack upon the metal base itself. Per unit period of time, the extent of attack is greater with the heavy scale; or to carry thru a definite operation, the total time lapse therefor may be increased. The specific instance above approximates 30% time saving.

Supplementing the foregoing is the resultant surface condition of the treated stock. The surface grain fineness approaches that of new stock so closely as to be almost indistinguishable therefrom. Absence of accelerator, under the disclosure herein, shows a most marked degree of roughness or pebbled face effect. In experiences for subsequent coating operations, such roughness or pebbling, as revealed in macrophotographs, involve many difficulties for establishing adequate surface anchoring, as well as failing to provide bases to carry attractive plating, coating, enameling and the like. There may be required less precision in performance to deliver a high grade merchantable output in applying the finishing coating upon the superior grade base, than when the character of the base be not so helpful. Accordingly the pre-treatment before coating, in which the accelerator of this invention be used, has worth in carrying thru for high grade finished products.

What is claimed and it is desired to secure by Letters Patent is:

A process of improving the surface condition of a metal in an acid pickling bath which consists in treating the surface of the metal to be pickled with a bath consisting of a pickling acid which is predominantly sulfuric acid and one to eight parts of sodium thiosulfate per seven hundred parts of 7% H_2SO_4.

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