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[54] **METAL-TREATING PROCESS**
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ABSTRACT: A method for treating steel, galvanized steel, zinc and aluminum sheet and strip with an HF-CrO₃ containing solution wherein the solution is applied so that no more than about 50 percent of the applied solution is returned to the treating bath and about 0.1–6 grams/square meter HF and about 0.06–3 grams/square meter CrO₃ are retained on the metal surface to give a pickling effect or metal removal of about 0.1 to 2 grams/square meter.

METAL-TREATING PROCESS

The present invention relates to an improved process for the chemical surface treatment of steel, galvanized steel, zinc and aluminum and more particularly relates to a process which is suitable for the preparation of these materials for the application of organic coatings.

It is known from Belgian Pat. No. 715,978 to pickle steel, zinc and aluminum with a solution containing 0.2 to 3 g./l. CrO_3 and 0.5 to 5 g./l. HF to such an extent that the metal quantity removed by the pickling will be 0.2 to 2 g./m.², and subsequently, to bring these materials in contact with an aqueous solution containing hexavalent chromium, in quantities of preferably 0.6 to 6 g./l. and calculated as CrO_3 , and then to dry the materials. The advantage of this process against the conventional processes is that the steel, zinc and aluminum are treated with only one solution and this will in no way impair the resistance characteristics of the subsequently applied organic coating layers, with respect to the specific surface treatment processes applied to the particular type of metal. As in this process only one treatment has to take place, unlike the conventional three phases of treatment. Therefore, the investment costs of the apparatus and the floor space requirements of the process are significantly reduced.

On the other hand, a drawback of the foregoing process involves a buildup of detrimental cations in the treatment solution. Thus a buildup of Fe-III ions will increase the corrosion attack on the steel and zinc surfaces. Furthermore, the corrosion resistance of the subsequently applied organic coating layers, such as, for example, lacquer coatings or polyvinyl chloride or polyvinyl chloride films, will be impaired. This detrimental effect upon corrosion resistance may be observed particularly with steel and aluminum and to a lesser degree also with zinc. Finally, through the increasing quantities of Fe-III, Al-III and Cr-III ions, significant quantities of active fluoride complexes will be tied up and therefore the pickling reaction will lose its efficiency. To overcome this drawback of the known process, it has been proposed that the buildup of these detrimental cations may be avoided by artificially increasing the mechanical losses of the bath, or by the utilization of a cation exchanger. Additionally, the continuously developing hexavalent chromium containing solutions and their subsequent antipollution treatment will require additional expenditures and involves considerable difficulties. Furthermore, the utilization of a cation exchanger is rather difficult due to the fact, that the Fe-III, Al-III and Cr-III ions in the pickling solution tend to give rise to only slightly dissociated fluoride complexes. Consequently, removal of these ions does not appear to be possible within economically feasible limits.

It was found, however, that in the chemical surface treatment of steel, galvanized steel, zinc and aluminum, particularly in the form of continuous strips or bands or in sheet form, the foregoing drawbacks may be avoided by pickling with a solution containing hydrofluoric and chromic acids, and by drying upon said surfaces a solution containing hexavalent chromium, through the application of an aqueous solution to the metal surface, said solution containing hydrofluoric and chromic acid, the application being carried out in such a manner that at most 50 percent, but preferably only 20 percent of the utilized solution will be returned into the treatment bath, and 0.1 to 6 g./m.² HF and 0.06 to 3 g./m.² CrO_3 will remain on the metal surface in order to give rise to a pickling effect of 0.1 to 2 g./m.².

The quantities of hydrofluoric acid and chromic acid required according to the method of the present invention are brought into contact with the metal surface in the form of an aqueous solution. The quantity of the solution and the conditions of application are so selected that at least 50 percent, but preferably 80 percent of the solution applied to the metal surface will remain upon that surface for the duration of the pickling reaction. In the conventional immersion or spraying process after the reaction with the metal surface more than 90 percent of the treatment solution will be returned to the storage tank and reused for the next phase of the process. The

remainder stays on the metal surface and will then be carried over into the rinsing tank. On the other hand, according to the method of the present invention at most only 50 percent of the pickling solution which comes into contact with the metal surface, but preferably only 20 percent of it will be returned to the storage tank and reused for the next pickling. In this manner any excessive buildup of detrimental cations will be substantially avoided. The buildup will decrease with decreasing quantities of solution which are recycled after the reaction.

The concentrations of hydrofluoric and chromic acid in the pickling solution, according to the method of the present invention, are desirably in the range of 5 to 30 g./l. HF and 3 to 15 g./l. CrO_3 . Usually, 20 to 400 ml./m.² aqueous solution is sufficient to ensure the application of the required HF and CrO_3 quantities to the metal surfaces. The lower quantities are appropriately applied when using higher concentrations of hydrofluoric-chromic acid solutions. These quantities, however, generally increase when the HF and CrO_3 concentrations are decreasing toward the lower limit.

The concentrations of HF and CrO_3 in the quantity of liquid applied to the metal surfaces should be so selected that under given temperature conditions and reaction times a pickling effect or metal removal of 0.1 to 2 g./m.² will be ensured. Below 0.1 g./m.² the roughening of the metal surface will be insufficient, therefore, adhesion difficulties may appear during subsequent coating with organic materials. On the other hand, pickling effects higher than 2 g./m.² will lead to the deposition of pickling residues, particularly on steel and aluminum, and this may be equally detrimental as far as the adhesion of organic coating layers is concerned. At the same time the consumption rate of the chemical ingredient will increase. With a pickling effect in the range of 0.1 and 2 g./m.² the metal surfaces will show a uniform roughening effect without any noticeable layer formation or pickling residues.

The pickling effect is also a function of the composition of the treatment solution, the temperature and the reaction time. The influence of the composition of the treatment solution, and therefore, the influence upon the pickling effect of the quantities of HF and CrO_3 applied to the metal surfaces may be seen from tables 1-3. To obtain these values in every instance 60 ml./m.² of the various pickling solution compositions were applied to steel sheet samples of UST 1405/m quality according to German Industrial Standard (DIN) 1623, page 1, also to galvanized steel samples with nonchromium treated surfaces and samples of aluminum quality AlMg₃. After 10 secs. of reaction time the solution film is rinsed off with water and dried. The pickling effect was determined from the weight difference of the sample sheets before and after the treatment.

Raising the temperature will accelerate the pickling reaction. Preferably the temperature of the pickling solution should be between 15° and 40° C., even though the process may be carried out at higher temperatures as well. The temperature, however, should not exceed about 60° C., as in this range it is rather difficult to control the desired pickling effect.

TABLE 1
[Pickling effect (g./m.²) on steel]

HF (g./m. ²)	CrO_3 (g./m. ²)			
	0.15	0.3	0.9	1.8
0.15	0.03	0.00	0.00	0.00
0.6	0.25	0.53	0.03	0.00
1.8	0.25	0.48	1.23	0.18
3.6	0.30	0.50	1.40	2.38

TABLE 2
[Pickling effect (g./m.²) on galvanized steel]

HF (g./m. ²)	CrO_3 (g./m. ²)			
	0.15	0.3	0.9	1.8
0.15	0.13	0.18	0.33	0.53
0.6	0.40	0.70	1.00	1.75
1.8	0.55	0.80	1.83	3.00
3.6	0.83	1.10	2.15	3.50

TABLE 3

[Pickling effect (g./m.²) on AlMg₃]

Hf (g./m. ²)	CrO ₃ (g./m. ²)			
	0.15	0.3	0.9	1.8
0.15-----	0.03	0.03	0.05	0.15
0.6-----	0.08	0.13	0.15	0.28
1.8-----	0.15	0.23	0.25	0.38
3.6-----	0.38	0.40	0.50	0.63

The pickling effect increases rapidly at first with increasing reaction time, but after about 10 to 30 seconds it will usually reach a limit which is a function of the composition of the solution, its temperature and the type of the metal as well. The increase of pickling effect with reaction time for steel is given in table 4. These results were obtained on weighed steel samples degreased with steam, and by applying 60 ml./m.² aqueous solution at 20° C., containing 5.3 g./l. CrO₃ and 10 g./l. HF, corresponding to 0.32 g./m.² CrO₃ and 0.60 g./m.² HF. Following the different extents of pickling times the samples were rinsed with water then dried and reweighed.

TABLE 4

	Reaction times (sec.)						
	1	2	3	4	5	10	30
Pickling effect (g./m. ²)-----	0.18	0.28	0.33	0.35	0.38	0.45	0.50

The process according to the present invention may be carried out by flooding, pouring or spraying as well as by roller application. When using the flooding or pouring process usually a higher recycling rate of the treatment solution from the metal surface into the storage tank should be taken into account. The recycled quantity, however, may be reduced by using less excess solution quantities and by distributing the solution on the metal surface in a uniform manner with rollers, squeezers or by some appropriate blowing arrangement.

When using the so-called roll-coat process, then practically 100 percent of the applied pickling solution will remain on the metal surface. This particular type of application should be carried out preferably by reverse coating. Altering the revolutions of the rollers or the relative speed of the application roller to the material to be treated, the thickness of the liquid film may be varied. The roll-coat process is less applicable to wavy metal sheets, as in this instance the treatment solution may not be applied uniformly. This may result in nonuniform pickling of the material which, under certain conditions, may give rise to a negative effect concerning the resistance characteristics of the subsequently applied organic coating.

In consideration of the foregoing difficulties, it is most appropriate to apply the solution to the metal surface by spraying. The diameter, the efficiency and the number of jets as well as the spraying pressure should be so selected that a uniform film will be formed on the metal surface, without any substantial quantities of solution passing by the treated material or running off. Generally, the distance between the jets and the metal sheet should be 10 to 25 cm. In order to obtain improved uniformity of the sprayed liquid film, several tubes provided with jets may be arranged in series, the jets being located at angles which will ensure uniformity. The reaction solution may be used directly from storage tank to metal surface without any dilution. On the other hand, a correspondingly higher concentrated solution may be injected into a water-fed spraying system. Here, the blending ratio of water to concentrate should be so adjusted that the solution which leaves the jets should have the desired concentration of CrO₃ and HF. This particular method of application will permit considerable volume reduction in the storage tank.

In the treatment of continuous strips or sheets the application of the pickling solution may take place either on the upper or on the lower surface of the materials or again simultaneously on both sides. With simultaneous application the

quantity of liquid applied to the upper or the lower side of the metal may be identical or not.

Whenever at least 80 percent of the applied solution remains on the treated surface, no special control of the composition will be required. On the other hand, when greater proportions are recycled from the metal surface, then from time to time the CrO₃ and free acid contents should be controlled by means of conventional analytical methods. The replenishment should be carried out preferably with CrO₃ to Cr (VI) consistency and with HF to free acid consistency. The replenishing materials may be added to the bath either individually or in premixed condition.

At the end of the pickling process, the excess solution remaining on the metal surface may be removed by squeeze rollers, a blowing arrangement or by some other appropriate devices, and the resultant solution film is dried. The prerequisite for this particularly advantageous method of operation is that the pickling solution should contain maximum 1 part by weight of HF per every part by weight of CrO₃. It should be particularly noted, that in this method of operation the two customary stages, i.e., the water rinse and the after-rinse with CrO₃ containing solutions will not be required, this again represents considerable savings on installations, floor space and expenditures otherwise required for the treatment of chromic acid containing effluents. When using the above-mentioned HF/CrO₃ ratio, under the given application conditions hexavalent chromium will be present in the pickling solution which is applied to the metal surface. When using higher HF and CrO₃ contents in the pickling solution, it is appropriate and particularly in the treatment of steel and zinc surfaces, that the HF/CrO₃ ratio should be adjusted to a value below 0.9 in order to ensure that after the reaction sufficient quantities of hexavalent chromium will remain on the surfaces. According to the method of the present invention, the solution film is removed from the metal surface to such an extent, e.g., by means of rubber squeeze rollers, that after drying a coating will be obtained which contains 6 to 120 mg./m.² hexavalent chromium, calculated as CrO₃.

According to another but similarly preferred embodiment of the method according to the present invention, the HF/CrO₃ ratio in the pickling solution is adjusted to values above 1. In this instance, in the treatment of steel and zinc surfaces under appropriate experimental conditions, for example under extended reaction times, and also in the treatment of aluminum, the total chromic acid quantities applied to the metal surface are being used up in the pickling reaction. The solution which remains after the reaction may be then removed by squeezing and/or water rinsing. As in this instance the solution does not contain any more hexavalent chromium, this solution may be immediately neutralized without any specific effluent treatment, therefore, the expenditures otherwise required for a chromic acid reduction process will be saved.

After the removal of the residual solution film from the metal surface or after rinsing with water, an aqueous solution containing Cr (VI) is used for after-rinsing, whereby 6 to 120 mg./m.² hexavalent chromium, calculated as CrO₃, will be applied to the surface. The solution is then dried. The Cr(VI) content of the solution calculated as CrO₃, should be preferably between 0.6 and 6 g./l., where the higher contents are used preferably whenever a squeezing process is employed to ensure the uniformity of the adhering solution film. The hexavalent chromium may be added to the bath for example in the form of chromic acid and/or zinc, calcium, aluminum and chromium-III-chromate. As far as the after-rinse is concerned, it is sufficient to bring the metal surface into contact for only a few seconds with the Cr(VI) containing solution. The temperature of the after-rinse may range from room temperature to about 60° C. Following the after-rinse, the liquid film remaining on the metal surface is dried. This may be followed by the application of lacquers, adhesives for plastic films and such.

The pickling solution, which contains CrO_3 and HF according to the process of the present invention, should be applied as far as possible to degreased surfaces. For degreasing the metal surfaces such well-known aqueous solutions of alkali cleaning agents are suitable which contain alkali hydroxides, alkali carbonates, alkali ortho and condensed phosphates, alkali silicates, alkali borates, complex-forming as well as surface active substances, and which may be applied to the metal surfaces by immersion, flooding or spraying and preferably at elevated temperatures. The degreasing process may be omitted whenever the metal to be treated is substantially grease-free, such as for example freshly galvanized steel. The process according to the present invention is particularly suitable for the treatment of continuous rolls and sheet metals. Nevertheless, it is also possible to treat objects of complicated shape such as for example auto body parts, refrigerator and washing machine housings and such. In this instance, however, it is appropriate to degrease the objects with low vaporizing solvents, for example chlorinated hydrocarbons. The objects should be then transported preferably into a chamber wherein an HF and CrO_3 containing aqueous solution is present in fine cloud dispersion. In this manner, the metal surfaces become uniformly coated with the pickling solution and the runoff of the solution is substantially avoided.

In order that those skilled in the art may better understand the method of the present invention, the following specific examples are given:

EXAMPLE 1

A 300-mm. wide steel band is treated in the following manner in a continuous arrangement:

a. Degreasing with an aqueous solution containing 3 g./l. NaOH 3 g./l. $\text{Na}_3\text{P}_3\text{O}_{10}$, 0.2 g./l. organic complex builder 0.7 g./l. nonionic emulsifier, 14 seconds spraying at 70°C ;

b. 4 seconds spray-rinsing with cold water;

c. After-degreasing with an aqueous solution containing 1.3 g./l. NaOH , 1.3 g./l. $\text{Na}_3\text{P}_3\text{O}_{10}$, 0.08 g./l. organic complex builder, 0.3 g./l. nonionic emulsifier, 14 seconds spraying at 70°C .; rinsing according to (b);

d. Pickling with a solution containing 5.3 g./l. CrO_3 and 10 g./l. HF , by spraying with 7 atm. pressure through two series of jets arranged above and below the steel band. The two jets are positioned alongside each other at a distance of 150 mm., and the distance of the jets from the steel band is 150 mm. The performance of the jets at 7 atm. pressure is 0.1 l./min. Flat spray jets are used with the angle of opening being 65° . Under these conditions, a liquid quantity of about 110 ml./m.² is applied to the steel band, of this quantity about 105 ml./m.², i.e., 95 percent remains on the surface. The solution film which contains 0.56 g. CrO_3 and 1.05 g. HF per m.² of sheet surface, is allowed to react for 8 secs. at 25°C .

A separate analytical investigation of the solution film upon the steel surface after 8 secs. of reaction time gave the following values:

CrO_3	not detectable
Cr (III)	2.3 g./l.
Total iron	5.5 g./l.
Fe (II)	1.1 g./l.
Fe (III)	4.4 g./l.

e. 4 sec. spray rinse with cold water;

f. After-rinse with an aqueous solution containing 3.4 g./l. CrO_3 , and 0.6 g./l. Cr (III) , 7 secs. spraying at 45°C ;

g. Squeezing with a rubber roller;

h. Drying in air circulation oven, 15 secs. at 85°C .

Following this treatment, the upper as well as the lower surface of the steel band have indicated clean, uniform and mat pickling effect. The content of hexavalent chromium was about 30 mg. CrO_3 per m.² of surface. Under the particular treatment conditions described in the foregoing, the pickling effect was evaluated on steel samples secured onto the steel band. These samples were the quality UST 1405 m. according to German Industrial Standard (DIN) 1623, page 1. The result was found to be in the range of 0.5 and 0.6 g./m.².

EXAMPLE 2

Samples of steel, hot galvanized steel and aluminum (AlMg_3) were degreased and rinsed with water in the manner described in example 1. Subsequently these samples were dipped for 1 sec. at 25°C . into a solution containing 5.3 g./l. CrO_3 and 10 g./l. HF . The HF/CrO_3 ratio was 1.9. The 60 ml./m.² solution film adhering to the samples after their removal from the solution was removed after an about 10 sec. reaction time, either by rinsing with water or by squeezing with rubber rollers. After the squeezing of the samples a solution film of 5 ml./m.² remained. On one portion of the samples this resulting solution film was dried. On the steel, hot galvanized steel and aluminum sheets, the presence of hexavalent chromium could not be detected.

The remainder of the samples were dipped into a solution containing 3.4 g./l. CrO_3 and 0.6 g./l. Cr (III) , for 8 secs. at 55°C . This solution was then squeezed off and the solution film of about 5 ml./m.² was dried for 3 minutes in an oven at 80°C . From the solution quantities remaining on the metal surface and the CrO_3 concentration, an about 15 mg./m.² CrO_3 content in the layer was ascertained.

In parallel experiments samples were pickled under identical conditions, however, with the exception that a 5.3 g./l. CrO_3 and 4 g./l. HF containing pickling solution was used (HF/CrO_3 ratio equals 0.76). The samples were squeezed with rubber rollers and dried. The CrO_3 content on the surface was found to be about 10 mg./m.².

The samples were subsequently lacquered by using a conventional lacquer of acrylate resin base. Following a storage period of 3 days, the samples were scratched and subjected to a salt-spray test according to ASTM B 117-64. The results of this test are given in table 5.

The data in this table clearly indicate that the corrosion resistance will significantly decrease when omitting the application of a chromate containing after-rinse when using an HF/CrO_3 ratio of 1.9, and thereby there will be no CrO_3 present on the surface. On the other hand, with an HF/CrO_3 ratio of 0.76 there will be still sufficient CrO_3 quantities present on the surface in order to produce satisfactory corrosion protection even without an after-rinse with a CrO_3 containing solution.

TABLE 5

HF/ CrO_3 ratio in the pickling solution:	After treatment			Penetration under the lacquer (mm.)		
	Squeezing	H_2O rinse	CrO_3 after rinse	Steel after 360 hr.	Zinc after 504 hr.	Aluminum after 5,000 hr.
1.9	+	+	+	3	3	4
1.9	+	+	+	3-4	3	3
1.9	+	+	+	3	1	4-5
1.9	+	+	+	7	15	10
0.76	+	+	+	3-4	4	3
(¹)	+	+	+	14	>15	9

¹ Degreased only with steam, for comparison only.

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EXAMPLE 3

Samples of steel, hot galvanized steel and AlMg₃ were degreased and rinsed in the manner described in example 1. These samples (series A) were pickled by an ordinary spray process, i.e., with a recycling ratio of over 90 percent, for 11 seconds at 25° C., using a solution containing 0.5 g./l. CrO₃ and 2.5 g./l. HF. Subsequently, the samples were rinsed, after rinsed and dried in the manner described in example 1.

In the course of a throughput experiment a total of 400 m.² steel surface per 100 l. of pickling solution was put through the bath. An ion exchange material was continuously added to the baths. The volume of the bath and the exchange resin were in 10:1 ratio. The pickling bath was replenished with CrO₃ and HF to constant CrO₃ and free acid content.

After about 150 m.² steel surface throughput per 100 l. bath solution, the ion exchange resin became saturated with Fe-III ions. After the total throughput of 400 m.² per 100 l. bath, an Fe-III content of 1.3 g./l. was found. At the same time, a second series of samples of steel, hot galvanized steel and AlMg₃ were pickled and after-treated in this bath in the manner described for series A (Series B).

For comparison purposes further samples of steel, hot galvanized steel and AlMg₃ (series C) were subjected to a spray treatment according to the process of the present invention. The experimental conditions were identical to those described in example 1 under treatment steps (a)-(h). The samples were arranged on a running steel band.

Some of the samples in Series A-C were lacquered with the

TABLE 6

	Penetration under the lacquer (mm.)			Penetration under the PVC film		
	Steel after 360 hr.	Zinc after 604 hr.	Alumi-num after 5,000 hr.	Steel after 360 hr.	Zinc after 360 hr.	Alumi-num after 360 hr.
Sheet series:						
A-----	3	3	4	3	1	0
B-----	6	4	5	5	1	1
C-----	2	3	3	1	1	0
(i)	13	>15	8	>15	>15	3

¹ Degreased only with steam, for comparison only.

acrylate resin lacquer customarily used for the lacquering of the steel bands, and another portion of the samples after the application of an adhesive were laminated with a hard-PVC-film.

The samples were prepared and tested in the scratched condition according to ASTM B 117-64.

The results are presented in table 6 in comparison with the results obtained from samples only degreased by steam and subsequently lacquered or laminated with PVC films.

What is claimed is:

1. A process for the chemical surface treatment of metals which comprises pickling the metal surface to be treated with an aqueous solution containing HF and CrO₃, applying said solution so that at least about 50 percent by volume remains on the metal surface, with no more than about 50 percent by volume being returned to the main body of the treating solution, retaining from about 0.1 to 6 grams/square meter HF and 0.6 to 3 grams/square meter CrO₃ on the metal surface and effecting pickling of the metal surface to the extent of removing from about 0.1 to 2 grams of metal/square meter of treated metal surface.

2. The process as claimed in claim 1 wherein at least about 80 percent by volume of the pickling solution is retained on the metal surface and no more than about 20 percent by volume is returned to the main body of the treating solution.

3. The process as claimed in claim 2 wherein the treating solution used has a maximum weight ratio of HF:CrO₃ of 1, which solution is applied so that after drying the solution on the treated surface, the resulting coating contains from about 6 to 120 milligrams/square meter of hexavalent chromium, calculated as CrO₃.

4. The process as claimed in claim 2 wherein after the desired pickling of the metal surface is obtained, the remainder of the treating solution is removed and the surface is thereafter treated with a second aqueous solution containing hexavalent chromium to form a coating which contains from about 6 to 120 milligrams/square meter of hexavalent chromium, calculated as CrO₃.

5. The process as claimed in claim 4 wherein the first treating solution used has a minimum weight ratio of HF:CrO₃ of 1.

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