NOVEL PICKLING ACID for the METAL FINISHING INDUSTRY

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INTRODUCTION

It is well known the importance of the surface preparation, especially in the Hot Dip Galvanizing process. It is also well known that the most effective and practical way to remove the oxides present on the steel is by a chemical reaction versus others mechanical methods. Nevertheless, the environmental problems associated with chemical descaling could limit their usage in closed or open tank processes.

Usually the galvanizing Industry uses Hydrochloric or Sulfuric acid, each one with some advantages and dissanvantages related to fumes, temperature requirements, energy consumption, metal attack, pitting, and Hydrogen embrittlement. Futher considerations such as the cost of recovery, neutralization, hazarous waste transportation and Super fund tax, creates a very difficult situation to decide which option is best choice for the operation.

Quimicos Inorchem, C.A., is a mayor distributor to the metal industry in Venezuela; Thus, we were motivated to conduct a research to develop a new pickling acid to minimize the problems associated with steel pickling.

At the same time we were concerned about the future of the acid supply and the environment, world wide, as we approach to the new millenium because the effect of the Chlorine and CFC'S in the ozone layer.

RESEARCH OBJECTIVES AND TECHNICAL APPROACH

- Minimize the Hydrogen Chloride Fumes;
- Minimizing the metal attack;
- Improve yield;
- Decrease pickling time.

Minimize the Hydrogen Chloride Fumes

We studied methods to modify surface tension and vapor pressure in comparison with the Hydrochloric acid, which has high vapor pressure of CLH↑ at room temperature. We combined in the new acid vapor pressure changes through inorganic salt combinations and biodegradable organic surface active agents, which dramatically reduced fuming.

Minimize the metal attack

Studies were conducted to determine the most effective organic surface active agents to create the neccesary barrier to minimize the metal attack, pitting, and Hydrogen embrittlement to enhance to the new acid composition.

Improved yield

To reach this objective we knew it was very important to maximize the results of the previous two objectives (fumes and metal attack) as these would result in a less acid consumption and longevity of the working solution. Nevertheless, we established precise composition ratio's by studies of collateral effects of the inorganic reactions and chemical interaction between the new acid components and some the ferrous compounds produced as the acid is depleted. This is a key factor in obtaining partial renewal of the "pickling potential" in the working solution. Thus, this feature also contributes to maintain less of gradient decrease in the working solution concentration.

Decreased pickling time

The new acid formulation proved, on average, to be more reactive than either Hydrochloric or Sulfuric Acid; therefore, it pickles faster over the life span of a bath. However, in order to improve pickling times during the life of a bath, it was immediately obvious that concentration and temperature studies to control the rate of reaction on oxides where necessary.

Químicos Inorchem,C.A has coined the term *"Thermal-Activation"* to describe the practice of thermal maintenance of a pickling solution in optimize pickling times and yield.

Thus, the new acid formulation allows us to start a new bath at a higher concentration at ambient temperature and than as the bath is worked to increase temperature. This is possible because of minimum fuming and assures the maintenance of pickling times and maximum yield.

FIELD TESTING RESULTS

Results of laboratory studies and through trials conducted on various types of Galvanizing operation in Venezuela who are now users of the new acid,"**GALVACID™**", i.e. Structures, Wire, Pipe, Grating, Continuos Strip and Small Parts:

The new acid met our previously mentioned objective reaching the same pickling time or faster than the Hydrochloric acid solutions (15-18% weight concentration) with minimum CLH↑ fumes generation, and decreasing up to three times the heated (160ºF) Sulfuric acid solutions (8-10% weight concentration) for the same propose. (See Graph 1&2)

We evaluated the significant decrease in the gradient of iron growth in the working solution in comparison with the traditional acids. (See Graph 4)

As we reach the objectives by focusing on vapor pressure and surface tension to reduce fuming we found that the concentration of the working solution can be increased without an appreciable increase in fume generation. This feature, as mentioned, has an important roll in the yield and pickling time. (See graph 3)

As we minimize the metal attack we also have less molecular Hydrogen that cause indirectly CLH↑ fumes.

PRACTICAL BENEFITS AND ADVANTAGES

There are an important amount of proccesing, economical, and environmental benefits as a result of the development of **GALVACID™:**

Minimized Fume Generation:

- Less acid consumption because we decrease over 200% the CLH↑ fume generation rate in comparison with the HCL at the same concentration;
- Significantly less corrosion in the plant buildings, structures, bridge cranes, electrical panels, and electronic controls with an important impact in the reduction of maintenance cost;
- A better work enviroment in the process area.
- A less impact for the outside enviroment.

Minimized Metal Attack:

- Acid consumption has been reduced by targeting the chemical reaction on the different layers of oxides present at the steel surface;
- Minimun pitting and Hydrogen embrittlement has been realized;
- As an consecuence of the hight level of "Metal surface conditioning" the new acid has demostrated the following improved process performance:

    1. Less dross generation,
    2. Better coating weight control,
    3. Improved Galvanizing Quality.

- Less ferrous compounds aglomeration, is another experience, in comparasion with the traditional acids preventing premature depletion. Thus, a working solution is never dumped by iron concentration considerations alone;

As we obtained the proper metal cleaning which is optimal **"Metal surface conditioning"** we over come some inefficiencies that occur in the degreasing stage. This feature has an important influence in reject reduction and also in better galvanizing quality.

Yield Increase

The combination of all the properties obtained in the new acid, and the use of **"THERMAL ACTIVATION**", in a low energy progression between 100ºF to 160ºF as solution ages, increases yield.

To document the yield increase we will mention some experiences by plants which previously used HCL:

HCL Plants

Country	Company	Type of galvanizing	Galvacid™ Temp.(ºF)**(2)**	Yield Kg. steel per Kg.**Galvacid™**	Yield vs. **(1)** AGA Survey HCL
Venezuela	Acerogrill	Grating	Room	50	30 %
Venezuela	Acerogrill	Grating	115 max.	70	80%
Mexico	Hylsa	Pipe	115 max.	67	73%

Note 1:
AGA Survey number for 26 Plants is 5.95 Gallons of HCL/ per Ton Steel Galvanized. It is equivalent to 38.61 Kg. of Steel / Kg. of HCl.

Note 2:
Temperature was applied after medium life of working solution.

H_2SO_4 Plant

The last experience we will mention is in the USA at Laclede Steel Plant in Fairless Hills, Pa. They previously used sulfuric acid solutions (10%) heated up to 160ªF. They have 3 pickle tubs and their average pickling time was 40-45 minutes. To conduct the trial they selected one pickle tub for the **GALVACID™** and immediately it was apparent that all the production could be handle with one tub. The pickling time was reduced to 15 minutes at the beginning and also was tested through a temperature range (110-160ªF). The over yield expected in comparison with sulfuric yield is approximately 300%. It is also important to note they have realized other benefits of less dross per ton galvanized, improved quality and better coating weight control. We will have more data in the near future as the trial progress.

Waste Reduction

As a direct consequence of the extra yield obtained, average field experience has shown reduction in waste:

- 35-45% versus the HCL Operation.
- 65-75% versus the H_2SO_4 Operation.

Increased Production

- As in the previous point the more yield and reduction in the pickling time will mean higher production rates over the production quantities. In the case of plants pickling with sulfuric acid the increase of production could be around 100% without any added capital investment.

Energy Savings

One of the more important advantages is Energy conservation:

- In the case of sulfuric operation the pickling solutions has to be heated continuously.
- The foam blanket produced in the operation with the new acid reduces the energy loss.
- Reducing the waste will save all the energy required to recover or to treat the effluent.
- Increasing the yield will save by reducing energy required for acid production as requirement decrease.

CONCLUSION

We have proven that through chemistry it is possible to improve conventional pickling performance. The new acid goes a long way toward addressing many of the problems associated with **"metal surface conditioning"** process considering his versatility, economical benefits and environmental advantages**.**