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METAL CLEANING

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The invention relates to processes and compositions for cleaning metal surfaces, and especially to the cleaning of metal surfaces in alkaline solutions by electrolytic methods for plating. It is particularly applicable to the electrolytic cleaning of metals in the bright nickel process of chromium plating.

In earlier chromium plating methods, the articles to be plated were first coated with nickel, then removed from the nickel solutions and buffed, and then introduced into the chromium plating bath. However, there has been developed a bright nickel plating process which produces a nickel surface upon which chromium can be plated directly without buffing. In this process the work to be plated is placed in racks having conducting portions spaced apart by insulating portions, and these racks carrying the articles are passed through an electrolytic cleaning bath, a nickel plating bath and a chromium plating bath with the customary intervening dips and rinses. In the chromium plating bath chromic acid works its way into the crevices of the insulating material and into other points of the racks from which even the most careful washing of the racks will not remove it entirely. As the same racks are then returned for reuse, they carry back very small amounts of chromic acid into the cleaning bath, no matter how carefully they may have been washed.

Some of the chromic acid so carried by the racks is removed by and introduced into the cleaning bath. When a certain extremely small concentration of chromic acid is reached in the alkaline cleaning bath (of course, in the form of sodium or potassium chromate), it forms, in some way not entirely understood, a chromate film of the surfaces of the metal articles. This film is not removed by the cleaning, and, while it is extremely tenuous, it is sufficient to prevent good adherence of the nickel to the base. Therefore, when the nickel is deposited on the article it cracks and peels off, so that unsatisfactory plating is obtained.

The art has known that this difficulty exists, and I have found that as little as .00034 gram of chromic acid per liter of cleaning solution is sufficient to prevent perfect adhesion, for example, upon a brass article which is cleaned by being made the cathode with a current density of 5 amperes per square decimeter for five minutes, as is a common practice in the art. A nickel layer deposited on such brass will appear to be perfect, but will peel when the article is deformed or when chromium is deposited on the nickel. The condition becomes worse as the amount of chromic acid is increased. In other words, a proportion of chromic acid amounting to 1 oz. in 22,000 gallons of solution in the cleaning bath will render proper plating impossible.

The art heretofore has known of only one solution for this problem, namely, to utilize the alkaline cleaning bath for such a limited period of time that the chromic acid concentration does not reach even the very small amount stated above. In many plants the cleaning solution must be thrown away once a day, even though such baths otherwise are usable for periods of from two to four weeks with only slight additions of cleaning material. It is evident that the waste of cleaning material under such conditions is enormous.

The object of the present invention is to provide a method and composition for cleaning metals, and particularly for cleaning metals which are to be chromium plated by the bright nickel process, which makes it possible to use an alkaline cleaning bath even though the chromic acid content exceeds by many times the amounts which normally will cause unsatisfactory plating.

It is a further object of the invention to provide a composition which, when dissolved in water, will give a cleaning bath which may be utilized for periods of time comparable to those for which the bath could be used for other metal cleaning purposes, in spite of the accumulation of chromic acid in the bath.

Another object of the invention is to provide a composition which, when dissolved, will have an inhibiting effect on the action of materials such as chromic acid over long periods. This is preferably accomplished by the mixture of a plurality of inhibiting agents, one of which has an inhibiting action as soon as it dissolves, while another only develops an inhibiting action slowly in alkaline solution.

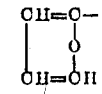
Further objects and advantages of the invention will appear more fully from the following description.

The basic concept of the invention is the addition to alkaline cleaning solutions of certain types of aldehyde materials. I have found that an inhibiting action is exerted by those aldehydes which do not, when in alkaline solution, polymerize to form insoluble condensation products. These aldehydes are those in which not more than one hydrogen atom is attached to the carbon atom in alpha position to the aldehyde group. As well as the aldehydes themselves, it is possible to use other compounds which yield or are con-

verted into this type of aldehyde in alkaline solution.

The aldehydes which are suitable for the purposes of this invention are those having the general formula RCHO, in which R is either:

1. Hydrogen.
2. The heterocyclic furyl group



its substitution products or its hydrogenation products.

3. A saturated aliphatic or hydroxyaliphatic group containing one or more carbon atoms in which none or not more than one valence bond of the alpha carbon atom is satisfied by a hydrogen atom, or

4. An aromatic group in which one or more of the hydrogen atoms attached to nuclear carbon atoms is replaced by a hydroxyl group.

It will be seen that all the aldehydes mentioned above either do not have an alpha carbon atom, as for instance in formaldehyde, or, if they do have such alpha carbon atom, do not have more than one valence bond thereof satisfied by a hydrogen atom. In other words, all such compounds contain not more than one hydrogen atom in alpha position to the aldehyde group.

As examples of the aldehydes which may be useful in the process, it should first be noted that only those which do not polymerize to resins which are insoluble or very slightly soluble in alkaline solution are useful. Among such compounds may be mentioned formaldehyde, paraformaldehyde, isobutyraldehyde, furfuraldehyde, hydroxyaldehydes, dimethanolacetaldehyde, salicylicaldehyde, and the like.

It is furthermore possible to use other compounds which do not conform to the above requirements, provided such compounds are converted in dilute alkaline solution into compounds of the required nature. Such compounds include both aldehydes and other substances such as carbohydrates or glucosides which break down in alkaline solution to form substances which possess an aldehyde structure. For example, glycollic aldehyde ($HOCH_2CHO$), which contains two hydrogen atoms on the alpha carbon atom, is converted in dilute alkaline solution by aldol condensation into trihydroxybutyraldehyde, which satisfies the requirements of the present invention.

Carbohydrates which contain an aldehyde group as well as those which do not may be useful, the latter apparently because they hydrolize or rearrange in alkaline solutions to form aldehydes. Some of these, however, require boiling in the alkaline solution for some time before they will become effective. Dextrose, mannose, fructose, pectin, maltose, lactose, d-levulose, and invert sugar among others are all effective in the process. Sucrose is also effective, but only after boiling for approximately eight hours to produce the invert sugar referred to above.

The starches also decompose in alkaline solutions to yield aldehyde compounds. Other materials which have been found to be effective in the process include pectin, agar agar, dextrine, gum tragacanth, Irish moss, gum arabic, quercitron, querbracho, myrabolans, sumac and the like.

The amounts of the different materials required for satisfactory inhibiting action vary of course with the quantities of chromic acid in the solution. The table below indicates for certain preferred types of compounds the quantity of inhibiting agent required to counteract varying amounts of chromic acid so as to obtain perfect adhesion of nickel to brass which had been cleaned in the solution. In all cases the test samples were made the cathode with a current density of 5 amperes per square decimeter. The solution contained alkaline cleaning materials in the following proportions, these being typical of the baths ordinarily used for cleaning metals, and being suitable for the practice of the present invention:

	Grams per liter
Sodium hydroxide	4.5
Soda ash	21.0
Trisodiumphosphate	4.5
Total	30.0

EXAMPLES

Grams of chromic acid per liter inhibited

Grams per liter of inhibitor	Furfuraldehyde	Dextrose	Dextrine	Starch	Maltose	Lactose	Pectin	Agar Agar
0.03	0.00051			0.00008				
0.45		0.00051						
0.6	0.0039			0.0010	0.00051	0.00051		
0.9				0.0020			0.0034	0.0017
1.2	0.0073	0.0039		0.0017				
1.5	0.0107			0.0024	0.0022	0.0022	0.0051	
1.8				0.0034				0.0051
2.1	0.0243	0.0073		0.0041				
2.4	0.0374	0.0083	0.0084	0.0041	0.0073	0.0056	0.0085	0.0068
2.7	0.0413			0.0041				
3.0	0.0544	0.0114		0.0085	0.0090	0.0090	0.0102	
4.5	0.102	0.0124	0.0068	0.0144				
6.0	0.163	0.0192						
7.5			0.0102					
9.0	0.289	0.0362						
10.5			0.0136					
12.0	0.425	0.0532	0.0204					
15.0	0.663	0.0804	0.0238					

It is obvious that one of the inhibiting agents used above will give tolerances of chromic acid as much as 2000 times those of the ordinary bath. For practical purposes, however, a tolerance of from 20 to 30 times that existing without the inhibitor is sufficient.

Similar results are obtained when other metals than brass are used as the base. The following table shows the inhibiting power of dextrose in a cleaning solution containing in addition to the composition described above .35 gram per liter of sodium oleate, when used for cleaning cold rolled steel. In this process the steel samples were made the cathode with a current density of 5 amperes per square decimeter.

Dextrose	Chromic acid
Grams per liter	*Grams per liter*
0.75	0.00051
1.2	0.0039
1.8	0.0073
2.1	0.0090
2.4	0.0107
3.0	0.0141
4.5	0.0175
6.0	0.0243
9.0	0.0481
12.0	0.0821
15.0	0.1195

According to the preferred embodiment of the invention, a mixture of two or more of the inhibiting agents is used. By combining a material which has a high initial inhibiting power

but which gradually loses a part of its effect, with a material which breaks down gradually in the alkaline solution to yield aldehyde compounds and thus increases in its inhibiting power it is possible to obtain solutions which give a more constant maximum tolerance. Apparently this is because the gradual decrease in power of one compound is offset by the gradual increase in the other. As examples, dextrose, or furfuraldehyde, which have immediate inhibiting power, may be mixed with starch or sucrose, which only have inhibiting power after they have been present for some time in the solution.

Certain mixtures have been found particularly effective for use in alkaline solutions as inhibitors. The following show very efficient combinations of materials, some of which are immediately effective while others become effective only after a time.

COMPOSITION 1

Furfuraldehyde	10
Dextrose	60
Starch	30

COMPOSITION 2

Dextrose	60
Sucrose	40

COMPOSITION 3

Dextrose	80
Furfuraldehyde	20

The latter composition is not as effective over long periods as the first two.

The inhibiting materials may be applied to alkaline solutions which have become contaminated beyond their normal tolerance for chromic acid, merely by adding an aldehyde inhibitor in a sufficient amount to raise the tolerance of the solution above the amount of chromic acid present therein.

In the cleaning processes of this nature, it is necessary to add alkaline materials to the cleaning solution at spaced intervals to replace losses of cleaning material from the bath. According to the present procedure it is desirable to combine the inhibitor with the alkaline materials in such proportions that the addition of the mixture to the solution will maintain the bath in a balanced condition and will preserve its inhibiting qualities. The proportion of chromate inhibitor to alkaline cleaning substances will vary in accordance with the condition of the racks and the care with which they are cleaned. Under the best conditions 10% of inhibitor and 90% of cleaning material may be used, but where the racks are not in good repair and are not properly washed it may be necessary to use equal quantities of cleaning material and inhibitor. Under usual conditions, from 10% to 25% of inhibiting material is sufficient.

Any well known type of alkaline cleaner may be used. The materials therein may comprise caustic soda, sodium carbonate, trisodium phosphate, sodium pyrophosphate, sodium orthosilicate, sodium metasilicate, sodium borate, or the corresponding potassium compounds, or mixtures of any of them. Soaps or soap substitutes which are essential at times in metal cleaners used for removing mineral oils may also be added. Such soaps preferably are sodium oleate or sodium resinate, and make up from ½% to 15% of the alkaline cleaners.

In preparing mixtures of this nature, it should be observed that conditions should be avoided which will permit the production of any substantial heat through the reaction between the alkaline substances and the inhibiting substances which might cause decomposition or other chemical change of the aldehyde compounds. When the products are to be in powder form the moisture content introduced as water of crystallization in the alkaline salts must be kept low so that no reaction will occur between the compounds in the dry state. When liquid aldehydes are used they must be combined with the alkaline materials by gradual addition and cooling so that no excess of temperature will occur.

The following are typical formulas of effective cleaning compounds having chromate inhibiting properties:

	Parts
4. Soda ash	30–70
Sodium pyrophosphate	5–25
Soap	0.2–20
Furfuraldehyde	5–20
5. Caustic soda	10–30
Sodium metasilicate	20–50
Trisodium phosphate	10–20
Dextrose	5–20
Starch	5–20
6. Sodium orthosilicate	50–80
Sodium rosinate	5–15
Dextrose	5–15

While I have described herein some embodiments of my invention, I wish it to be understood that I do not intend to limit myself thereby except within the scope of the appended claims.

I claim:

1. In a bright nickel process of chromium plating metal which comprises first plating the metal with nickel and then with chromium from a chromic acid solution, the step of cleaning the metal before plating with nickel by exposing the same to electrolytic action in an alkaline solution containing a chromate film inhibiting agent selected from the group consisting of compounds containing an aldehyde group and having not more than one hydrogen atom in alpha position to the aldehyde group and compounds capable of yielding such aldehyde compounds in alkaline solution.

2. In a bright nickel process of chromium plating metal which comprises first plating the metal with nickel and then with chromium from a chromic acid solution, the step of cleaning the metal before plating with nickel by exposing the same to electrolytic action in an alkaline solution containing furfuraldehyde.

3. In a bright nickel process of chromium plating metal which comprises first plating the metal with nickel and then with chromium with a chromic acid solution, the step of cleaning the metal before plating with nickel by exposing the same to electrolytic action in an alkaline solution containing a plurality of chromate film inhibiting agents selected from the group consisting of compounds containing an aldehyde group and having not more than one hydrogen atom in alpha position to the aldehyde group and compounds capable of yielding such aldehyde compounds in alkaline solution, one of said agents having inhibiting properties immediately upon solution in water, and another developing such properties only after solution for a period of time in alkaline solution.

4. A process as claimed in claim 3 in which said agent having inhibiting properties immediately upon solution in water is furfuraldehyde.

5. A process as claimed in claim 3 in which said agent having inhibiting properties immediately upon solution in water is furfuraldehyde and said agent developing such properties only after solution for a period of time in alkaline solution is starch.

6. A bright nickel chromium plating process which comprises placing articles to be plated in carriers, passing such carriers and articles successively through and subjecting them to electrolytic action in an alkaline cleaning bath containing a chromate film inhibiting agent comprising at least one substance from the group consisting of compounds containing an aldehyde group and having not more than one hydrogen atom in alpha position to the aldehyde group and compounds capable of yielding such aldehyde compounds in alkaline solution, a nickel plating bath and a chromium plating bath, removing the articles from the carriers, placing unplated articles in the carriers, and passing such unplated articles and carriers successively through and subjecting them to electrolytic action in the same baths.

7. A composition for electrolytically cleaning metal surfaces before electroplating with nickel and then with chromium comprising a water soluble alkaline cleaning material and a plurality of chromate film inhibiting agents selected from the group consisting of compounds containing an aldehyde group and having not more than one hydrogen atom in alpha position to the aldehyde group and compounds capable of yielding such compounds in alkaline solution, one of said agents having inhibiting properties immediately upon solution in water, and another developing such properties only after solution for a period of time in alkaline solution.

8. A compound as claimed in claim 7 in which said agent having inhibiting properties immediately upon solution in water is furfuraldehyde.

9. A composition for electrolytically cleaning metal surfaces before electroplating with nickel and then with chromium comprising a water soluble alkaline cleaning material and a plurality of chromate film inhibiting agents comprising furfuraldehyde and starch.

10. A composition for electrolytically cleaning metal surfaces before electroplating with nickel and then with chromium from a chromic acid solution comprising a water soluble alkaline cleaning material and a chromate film inhibiting agent selected from the group consisting of compounds containing an aldehyde group and having not more than one hydrogen atom in alpha position to the aldehyde group and compounds capable of yielding such compounds in alkaline solution.

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