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REGENERATION OF EXHAUSTED CHROMIUM BATHS

Method of regeneration of exhausted chromium baths produced during chroming and copper removal was developed. The method consists of electrochemical oxidation of Cr(III) to Cr(VI), dilution of the bath with demineralized water in 1:1 ratio and removal of copper ions by ion exchange method.

Dimensions of the column allowed application of the results obtained to industrial conditions. The regeneration of resin bed was carried out with 10% sulphuric acid. A decrease in consumption of sulphuric acid necessary for regeneration of resin bed by about 80-90% is possible by the recovery of copper from its solutions applying electrochemical reduction.

The results obtained proved that the method proposed allows regeneration of the exhausted chromium bath, enabling thus reapplication in chroming and copper removing.

1. INTRODUCTION

The investigations aim at developing a new technology for the regeneration of plating baths by an ion exchange combined with an electrochemical method. The most commonly methods applied today consist in treating the exhausted chromium baths mainly by reduction of Cr(VI) to Cr(III) and its removal in the form of a sediment [1]-[3]. Their major disadvantage is the waste of precious raw material and the pollution of the environment with toxic substances stored on dumping grounds that are not suitable for that purpose.

2. METHODS AND RESULTS

Exhausted baths from chromium plating and copper removal processes were investigated. Their composition was as follows: Cr(VI) - 242 g/dm³, Cr(III) - 42 g/dm³ and Cu(II) - 68 g/dm³. High concentration of Cr(III) would result in the rapid exhaustion of the resin bed in the ion exchange column. Therefore, before introducing the bath into the resin column, Cr(III) was electrochemically oxidized to Cr(VI). Parameters of the process were

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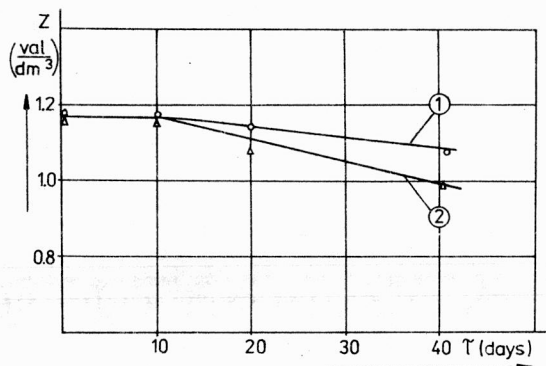


Fig. 1. Exchange capacity of Wofatit KS-10 depending on the time of contact with bath
curve 1 - diluted bath (1:1), curve 2 - undiluted bath



Fig. 2. Photos of Wofatit KS-10 taken under ZETOPAN microscope of Reichert production, enlarged 80 times after passing undiluted bath liquor through the column

as follows: anode current density - 1.8 A/dm^2 , cathode current density - 50 A/dm^2 , temperature - $80\text{--}82^\circ\text{C}$.

In the investigations, resin Wofatit KS-10 (GDR production) was used. Experiments on the resistance of the resin to oxidizing effect of the bath showed that it should be diluted with demineralized water in 1:1 proportion before being passed through the resin column. Undiluted chromium bath liquor causes a much larger decrease in exchange ca-

capacity than the diluted one. The results obtained are presented in fig. 1. They were also confirmed by microscopic examination of resin grains (fig. 2). In some grains numerous cracks were formed as the result of the oxidizing effect of the undiluted bath. Such changes were not observed when diluted liquor was used. It is recommended to dilute the bath with rinsing water coming from the column at the end of the regeneration. The bath after dilution was passed through the ion exchange column filled with 0.5 dm^3 of resin. Dimensions of the column ($\phi = 40 \text{ mm}$ and $h = 1000 \text{ mm}$) allowed application of the results to industrial conditions.

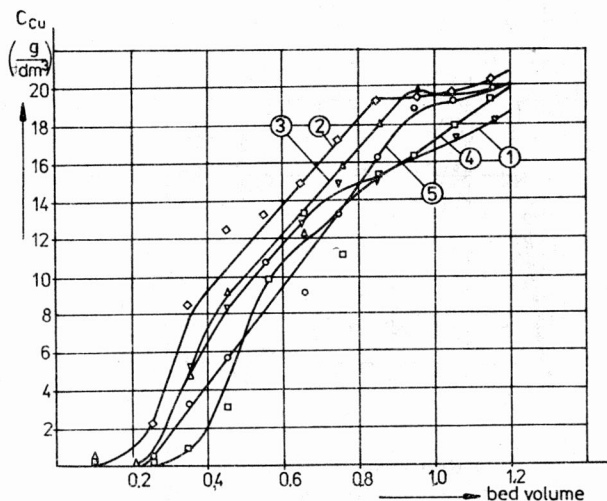


Fig. 3. Ion exchange curves ($\text{H}^+/\text{Cu}^{2+}$) during individual working cycles of resin
curve 1 – one cycle, curve 2 – 5 cycles, curve 3 – 10 cycles, curve 4 – 15 cycles, curve 5 – 20 cycles

Concentrations of Cu(II), Cr(III) and Cr(VI) were determined in the effluent from the column. One of the most important parameters characterizing the ion exchange process is the loading of the resin column. In the range from 14 to $36 \text{ dm}^3/\text{h}/\text{dm}^3$ of resin there was not observed any effect of column loading on the dynamics of $\text{H}^+/\text{Cu}^{2+}$ exchange. Stability of the resin used and the process of ion exchange were investigated in 20 working cycles of the resin column. One cycle comprised ion exchange process, regeneration of the ion exchange bed and repeated rinsing until a neutral reaction of effluent was achieved.

The dynamics of the $\text{H}^+/\text{Cu}^{2+}$ exchange in individual cycles at a column loading of $14 \text{ dm}^3/\text{h}/\text{dm}^3$ of resin was determined (fig. 3). Since the breakthrough curves do not differ, it may be concluded that the resin can be used for a minimum of 20 cycles, which in most plating plants allows them to be exploited for about 2 years. The regenerated bath after its concentration could be reused.

Multiple usage of the resin requires its regeneration by means of 10% sulphuric acid. Based on the results obtained, the curves characterizing the dynamics of $\text{Cu}^{2+}/\text{H}^+$ exchange were drawn (fig. 4). As can be seen, there are no changes in the course of regeneration of the resin bed during individual working cycles. This indicates that the working capacity of the column does not decrease during the operation.

In order to reduce the consumption of sulphuric acid needed for regeneration of the

resin, an electrochemical method was applied. It allows simultaneous recovery of copper from post-regeneration solution containing Cu(II) ions in mean concentration of 11 g/dm^3 and Cr(III) in concentration of about 0.5 g/dm^3 .

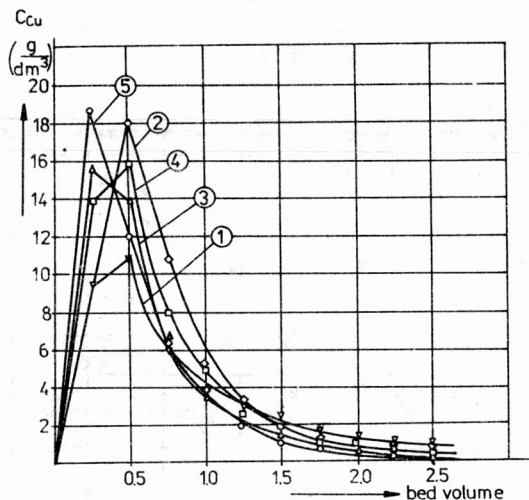


Fig. 4. Regeneration of spent resin with 10% H_2SO_4

curve 1 – after one cycle, curve 2 – after 5 cycles, curve 3 – after 10 cycles, curve 4 – after 15 cycles, curve 5 – after 20 cycles

Investigations into the removal of copper ions were carried out in a 350 cm^3 electrolyzer. Copper plate of 1 dm^2 surface area was used as a cathode, whilst the anode was made of lead sheet. Reduction of copper ions was carried out under potentiostatic conditions. Cathode potential measured against a saturated calomel electrode was 190 mV . This potential value allowed a required current density, i.e. current being 30–40% of its limiting value, at a given concentration of copper ions. At the concentration of about 11 g/dm^3 the initial current density was about 0.8 A/dm^2 . During the reaction, the concentration of copper ions and the current value decreased at a constant potential. Typical changes in parameters and calculated values characterizing the investigated reaction are presented in the table.

As follows from the data presented in the table, current density at a constant potential decreases with decreasing concentration of copper ions. In order to use electric energy in a proper way, cascade changes in current intensity should be applied in the process (carried out at uncontrolled potential). The values of current density in the case discussed are 0.77 A/dm^2 , 0.62 A/dm^2 and 0.47 A/dm^2 for varying concentrations of copper ions in the ranges $12\text{--}8 \text{ g/dm}^3$, $8\text{--}6 \text{ g/dm}^3$ and $6\text{--}2.5 \text{ g/dm}^3$, respectively. At the current densities mentioned above, electric charges of 3.6 Ah/dm^3 , 6 Ah/dm^3 and 9 Ah/dm^3 passed through the system. Under these conditions recovery of copper from solutions after resin regeneration ensures a good quality of copper plate at energy consumption of $1.7\text{--}1.9 \text{ kWh/kg}$.

Table

Observed (1-4) and calculated (5-7) parameters determined during removal of copper from a post-regeneration solution

t (s)	I (A)	E (V)	V (V)	Q (Ah)	e (Wh/g)	c (g/dm ³)
1	2	3	4	5	6	7
600	-0.784	-0.124	1.67	0.13	1.6	11.6
1200	-0.753	-0.140	1.842	0.26	1.7	11.2
1800	-0.817	-0.134	1.849	0.39	1.7	10.8
2400	-0.787	-0.164	1.868	0.52	1.8	10.3
3600	-0.772	-0.191	1.891	0.79	1.8	9.5
4800	-0.769	-0.185	1.892	1.03	1.8	8.7
6000	-0.636	-0.190	1.890	1.25	1.8	8.0
7200	-0.639	-0.195	1.893	1.47	1.8	7.3
8400	-0.621	-0.178	1.894	1.67	1.8	6.7
9600	-0.521	-0.185	1.881	1.86	1.7	6.1
10 800	-0.588	-0.176	1.887	2.04	1.7	5.5
12 000	-0.499	-0.179	1.878	2.20	1.8	5.0
13 200	-0.495	-0.193	1.888	2.37	1.8	4.4
14 400	-0.470	-0.190	1.880	2.52	1.8	3.9
15 600	-0.432	-0.174	1.865	2.68	1.7	3.4
16 800	-0.423	-0.172	1.867	2.83	1.7	3.0
18 000	-0.424	-0.182	1.868	2.97	1.7	2.5

Removal of copper from the solution of sulphuric acid used for regeneration of the resin enables multiple application of 80-90% of initial volume of the acid in the process.

3. CONCLUSIONS

The suggested method of regeneration of exhausted chromium baths is presented schematically in fig. 5. It permits multiple reuse of chromium baths in chroming plating and copper removal processes. Thus, it is possible to decrease considerably the consumption of chromium compounds in plating plants and to protect the environment by decreasing the discharge of noxious wastes, toxic to the soil and waters. A 80-90% decrease in the

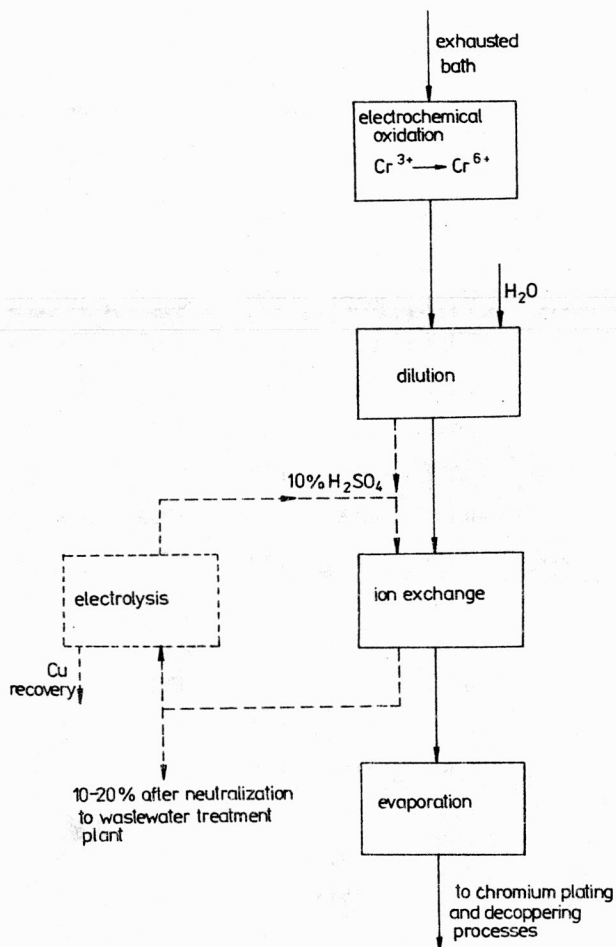


Fig. 5. Schematic of the regeneration process of exhausted chromium baths

consumption of sulphuric acid, necessary for regeneration of resin bed, is possible by the recovery of copper from the post-regeneration solutions, applying electrochemical reduction.

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REGENERACJA ZUŻYTYCH KĄPIELI CHROMOWYCH

Przedstawiono metodę regeneracji zużytych kąpeli chromowych pochodzących z procesów chromowania i odmiedziowywania. Metoda ta polega na elektrochemicznym utlenianiu Cr(III) do Cr(IV), a następnie – po rozcieńczeniu zużytej kąpeli chromowej w stosunku 1:1 – usunięciu jonów miedzi na jonicie typu Wofatit KS-10. Badania wykonano w kolumnach jonitowych pozwalających na przeniesienie uzyskanych wyników badań na skalę przemysłową. Do regeneracji złoża jonitowego stosowano 10% kwas siarkowy. Celem zmniejszenia jego zużycia zastosowano elektrochemiczny odzysk miedzi z roztworów poregeneracyjnych. Wykonane badania dowiodły, że przeważająca ilość kwasu siarkowego (około 80–90%) może być ponownie użyta do regeneracji złoża jonitowego. Wyniki badań wskazują, że zastosowana metoda pozwala na regenerację zużytej kąpeli chromowej w stopniu umożliwiającym jej ponowne użycie w procesach chromowania i odmiedziowywania.

РЕГЕНЕРАЦИЯ УПОТРЕБЛЕННЫХ ХРОМОВЫХ ВАНН

Представлены методы регенерации употребленных хромовых ванн, происходящих из процессов хромирования и отделения меди. Этот метод состоит в электрохимическом окислении Cr(III) к Cr(IV), а затем – после разбавления употребленной хромовой ванны в пропорции 1:1 – удалении ионов меди на ионите типа Wofatit KS-10. Исследования были выполнены в ионитовых колонках, позволяющих отнести полученные результаты к промышленному масштабу. Для регенерации ионитового слоя применяли 10% серную кислоту. С целью уменьшения ее употребления применили электрохимическое восстановление меди из послерегенерационных растворов.

Выполненные исследования доказали, что большая часть серной кислоты (около 80–90%) может быть употреблена повторно для регенерации ионитового слоя. Результаты исследований показывают, что примененный метод позволяет регенерировать употребленную хромовую ванну в такой степени, которая дает возможность повторного применения в процессах хромирования и отделения меди.