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ELIMINATION *IN SITU* OF NO_x EMISSION IN INDUSTRIAL SOLUTIONS FOR POLISHING OF COPPER ALLOYS

New pickling solutions (the CuNOX type baths) for the chemical polishing of brasses and other copper alloys, permitting the neutralization of nitrogen oxides (NO_x) directly in the bath, have been described. The use of the new and conventional baths has been compared in terms of evolution of NO_x gases in laboratory and industrial conditions. The CuNOX baths practically stopped the emission of nitrogen oxides during bright pickling.

1. INTRODUCTION

The majority of the processes of chemical treatment of metals is connected with the emission of various toxic gases and acid vapours. The solutions of nitric acid, most often with different admixtures, are applied for chemical brightening of copper and its alloys, such as brasses. As a result of the reaction of nitric acid with copper or other metals, which are contained in pickled alloys, relatively large amounts of toxic nitrogen oxides, mainly NO and NO₂ (NO_x), are formed [1], [2]. The necessity of applying the chemical polishing of copper alloys in various technological processes hinders a proper air-tight sealing of pickling tanks as well as a proper neutralization of NO_x [3], [4]. This paper presents the properties of a new generation of polishing solutions, the CuNOX type baths, which permit the neutralization of the NO_x to be performed directly in the pickling solutions, pickling without the NO_x evolution.

2. EXPERIMENTAL PROCEDURE

The chemical compositions of the pickling solutions chosen to be studied are listed in tab. 1. The electrolyte was prepared from chemically pure substances and distilled water. First of all the solid substances were dissolved in water, then the acids

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Table 1

Compositions of solutions used for bright pickling (chemical polishing) of copper alloys

Substances	Solutions			
	I [1], [2]	II [1], [2]	III [8]–[10]	IV [7]
HNO ₃ , 15 N, (m ³)	0.340	0.900	0	0.450
H ₂ SO ₄ , 36 N, (m ³)	0.330	0	0.430	0
H ₂ O, (m ³)	0.330	0.100	0.570	0.550
Others	+Cl ⁻	+Cl ⁻	+CO(NH ₂) ₂ +NH ₄ NO ₃ +Si _n (OH) _m +Cl ⁻	+CO(NH ₂) ₂ +(NH ₄) ₂ SO ₄ +R ₁ R ₂ SO ₂ +Cd ²⁺ , Cl ⁻

were added. The effects of different copper alloys (commercial chemical compositions) on the evolution of the NO_x during pickling in various solutions were examined. These alloys were copper (99,6%), α-brasses (CuZn37 and CuZn10) and multi-phases brasses, leaded α+β' brass (CuZn39Pb2), tin brass (CuSn10) and aluminium iron brass (CuAl10Fe3). The alloys for laboratory investigations were machined into cylindrical samples 2.5 cm long and 0.50 cm gauge diameter. The procedures of determination of NO_x (NO+NO₂) gases were the same, as described in other sources [5]. Measurements of NO_x emission during pickling of those alloys were conducted in a glass cell (1500 cm³) containing 250 cm³ of the pickling mixture. During the investigations, the samples were immersed in the pickling solution for 100

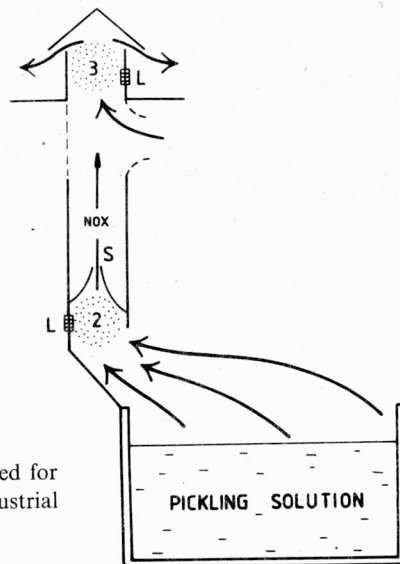


Fig. 1. Schematic layout of the plant tank used for the bright pickling of brass articles on an industrial scale

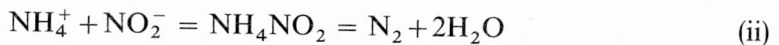
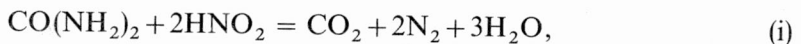
L - air-lock, S - slot

s and then taken out. The nitrogen oxides generated during the pickling were subsequently taken out at intervals and retained in the absorption bulbs.

The investigations of the NO_x emission under industrial conditions were carried out by means of polish pickling of the brass CuZn39Pb2 fittings whose surface was strongly polluted with the products of thermal grease destruction and graphite. These parts were made by means of hot forging, the average weight of pickled elements was about 100 g. The pickling was performed in a 1.0 m³ tank. The brass was pickled in the austenite steel basket, about 80 kg in one operation. Figure 1 presents the layout of the tank construction and lateral exhaust hoods with the points at which the NO_x concentrations were analysed. The NO_x content was analysed by means of indicator tubes (Drägerwerke, West Germany), in the area no. 1. The air and NO_x mixture was taken by the air-locks *P* from the points marked on the diagram (fig. 1) as 2 and 3 to the glass bottles of 500 cm³ volume. The time of bottling by negative pressure was 2 s. The NO_x content in the air of these bottles was measured by ordinary laboratory methods [5], [6].

3. RESULTS AND DISCUSSION

The solutions for bright pickling of copper alloys, especially brasses, which are most often applied in the industry, are based on the solutions of strong acids in the presence of the nitrate ion. The NO_3^- ion is most often introduced in the form of nitric acid. The solution I (tab. 1) is most often used for the pickling of homogeneous alloys (brasses α), the alloys of a relatively high copper content. The surface of the pickled alloys should be degreased. The solution II is used for pickling of brasses, including also heterogeneous brasses of strongly impured surfaces. The high concentration of nitric acid enables the details (parts) to be pickled without initial degreasing, for example castings or hot forgings. The solution III (CuNOX-2) has similar properties to solution I, while the bath IV is similar to the solution II. The elimination of emission in these baths was obtained by the decomposition reaction of the NO_2^- anion with urea and ammonium compounds, according to the reactons:



The proper choice of other additions contributed to the appropriate pickling velocity and process efficiency [7]–[10].

The chemical polishing in the solutions III and IV contributes to a very high rate of surface polishing definitely not worse than this in the baths I and II, respectively. The CuNOX solutions cause slight local stainings of the alloy surface as a result of the copper cementation reactions occurring during rinsing. This effect helps to

increase the time necessary for the removal of pickled details from the pickling bath to rinsing water. The increase of the time of pickling in the CuNO_x baths and the lower susceptibility to cementation enable the mechanization of pickling to be undertaken.

Table 2 presents the mean values of the emission of nitrogen oxides (converted into NO₂) during chemical polishing of different alloys in the solutions given in tab. 1. On the basis of the data presented it can be stated that during the pickling in comparable conditions and in the optimum temperature, in a given bath the NO_x emission may be decreased by 300–900 times. The observed differences in the amount

Table 2.

Average emission of the nitrogen oxides ($\text{cm}^3_{\text{NO}_2}/\text{m}^2\text{s}^{-1}$) during the laboratory chemical polishing of copper alloys in various solutions

Alloys	Solutions			
	I — 310 K	II — 320 K	III CuNO _x -2 315 K	IV CuNO _x -1 315 K
Cu	1800	2700	2	5
CuZn39Pb2	2500	3100	4	8
CuZn37	2400	3000	3	6
CuZn10	2000	2700	3	5
CuSn10	2800	3400	7	12
CuAl10Fe3	2000	2500	4	5

of the nitrogen oxide emission, measured in laboratory conditions, result from differences in the dissolving rates of the alloys tested. A higher dissolving rate causes an increased consumption of a pickling bath and thus, proportionally, an increased NO_x emission. Under industrial conditions the investigations of the NO_x emission were carried out using the equipment shown schematically in fig. 1. The leaded brasses were pickled in a 1.0 m³ tank for 100 s and the removal of the pickled charge from the pickling bath to water lasted 20 s. Rinsing lasted 40 s. The course of pickling is illustrated in fig. 2. The tank was ventilated during pickling. The air flow velocity in the intake of removed gasses (area 2) was 0.5 m/s. Taking into account the tank dimensions and cross-section of ventilating pipes, the ventilation rate for the used exhaust hoods was established as 0.7 m³/s, as converted to 1 m² of the pickling tank area. The volume of the NO_x emission (the dependence presented in fig. 3, measured in the area 2, fig. 1) depends on the time of pickling and rinsing. In the time of pickling, i.e., when the pickled brass parts were immersed in the pickling solution, it grew slightly and was 4–6 mg/m³. The application of a conventional pickling solution (concentrated nitric acid) resulted in the emission of 120–600 mg/m³ of NO₂ in comparable conditions. The removal of the basket from the pickling solution

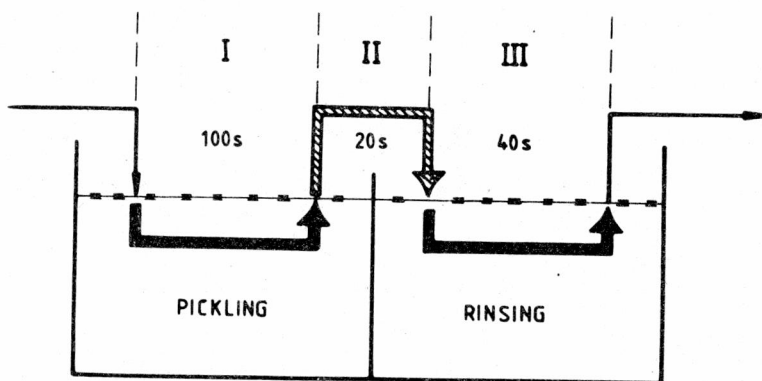


Fig. 2. Illustration of the pickling and rinsing process

caused in both analysed cases a significant increase of the emission of nitrogen oxides. For the bath CuNOX-1 this increase was relatively small, and the rise of the NO_x formation was manifested by the concentration increase up to about $13 \text{ mg of NO}_2/\text{m}^3$ in the analysed area 2 (fig. 1). In comparable conditions, during removing the brass samples from the concentrated nitric acid to water, the NO_x emission was exceptionally large, about 1000 mg/m^3 and more. The effect of the increased emission in the range II, marked in fig. 3, corresponds to the period connected with the removal of the brass samples from the acid to water. In this time a distinct increase of temperature occurs on boundary between the pickling solution and the metal which promotes the rate of the alloy dissolution. In the air, cooling is delayed and the dissolving reactions are strongly exothermic. In elevated temperatures (323K and more) the decomposition of the nitrite ion also hindered as a result of its reaction with ammonia ions as well as with urea.

In the vicinity of the pickling tank, where the workers usually remain, the concentration of nitrogen oxides was measured during 6 hours every half an hour. In the time of brass pickling in a conventional bath (bath II, tab. 1) the air pollution by nitrogen oxides was relatively high, from 3 to 15 mg/m^3 , 10 mg/m^3 on average which denotes the exceeding of a threshold limit, i.e., 5 mg/m^3 . Then the CuNOX-1 bath was applied, the air pollution by nitrogen oxides ($\text{NO} + \text{NO}_2$) in the area 2 (fig. 1) was significantly lower and equaled from 0 to 2 mg/m^3 , 0.5 mg/m^3 on average.

The efficiency of the new pickling technology (CuNOX-1) was also measured by determining the NO_x emission at the exit of the chimney drawing the gases from the pickling room. The measurements were carried out in the place 3 (fig. 1). When analysing the gases emitted, it has been stated that the air drawn from the surface of the pickling tank constitutes about 20% of the gases, the rest is the air from other parts of the pickling room, practically without nitrogen oxides. The mean emission (measurements every hour in the 4 hour cycle) was 2 mg/m^3 when the CuNOX-1 bath was applied. The bright pickling with the use of the solution based on the nitric

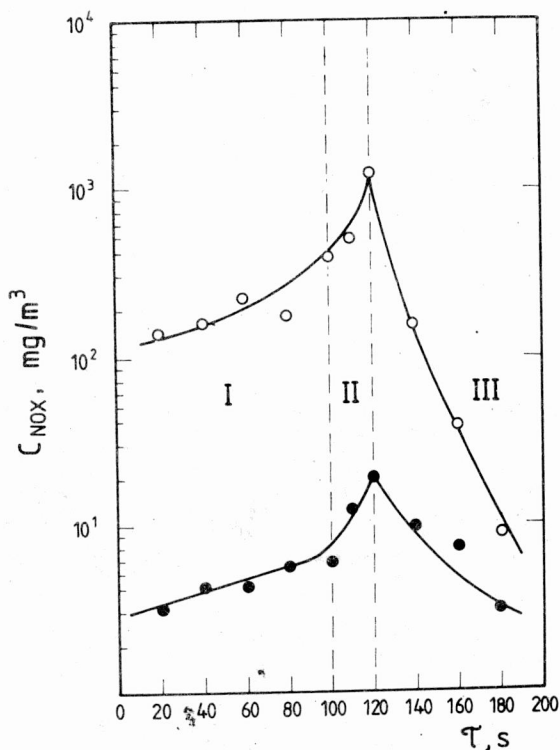


Fig. 3. Emission of the nitrogen oxides (NO_x) during the pickling and rinsing processes conducted in the vicinity of the pickling bath (area 2, fig. 1)

Closed circle — bath no. IV (tab. 1, CuNOX-1), open circle — bath no. II (tab. 1, concentrated HNO_3)

acid (bath II, tab. 1) resulted in a high emission, 200 mg/m^3 on average. Those results denote that NO_x evolution in the CuNOX-1 technology is approximately 100 times lower than in the traditional method.

4. CONCLUSIONS

In the new CuNOX type baths for the bright pickling (chemical polishing) of the copper alloys, especially brasses, the evolution of nitrogen oxides practically have been stopped. A very low emission of nitrogen oxides promotes the industrial application of this method without the necessity of using the installations neutralizing the NO_x gases. These baths can be applied under all production conditions because chemical brightening during pickling in standard tanks has been carried out. The properties of the CuNOX baths allow the ecologically clean polishing technology to be introduced also to these plants in which it is impossible to apply neutralizing devices because of technological and economical reasons.

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ELIMINACJA EMISJI TLENKÓW AZOTU
W PROCESIE POLEROWANIA STOPÓW MIEDZI

Opisano nowy rodzaj roztworów trawiących (kąpiele typu CuNOX) stosowanych w procesie chemicznego polerowania stopów miedzi. Kąpiele tego typu pozwalają na neutralizację tlenków azotu bezpośrednio w kąpielu. Porównano wykorzystanie nowych i konwencjonalnych kąpeli biorąc pod uwagę wydzielanie się tlenków azotu w warunkach laboratoryjnych i przemysłowych. Stwierdzono, że zastosowanie kąpeli typu CuNOX praktycznie likwiduje emisję tlenków azotu w czasie procesu polerowania.

ЭЛИМИНАЦИЯ ЭМИССИИ ОКИСЛОВ АЗОТА
В ПРОЦЕССЕ ПОЛИРОВКИ МЕДНЫХ СПЛАВОВ

Описан новый вид травильных растворов (ванны типа CuNOX), применяемых в процессе химической полировки медных сплавов. Ванны такого типа способствуют нейтрализации окислов азота непосредственно во время полировки. Сравнено использование новых и конвенциональных ванн, принимая во внимание выделение окислов азота в лабораторных и промышленных условиях. Было установлено, что применение ванны типа CuNOX практически элиминирует эмиссию окислов азота во время процесса полировки.