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New passivating pastes for stainless steel without nitric acid

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Abstract

Handled stainless steel (SS) structures often need accurate passivating treatments before use. Until now the most frequently used passivating pastes have been based on nitric (fluoridric) acid and, as a result, are responsible for consequent environmental problems. This work addresses the SS passivation quality of two low environmental impact pastes, based on peroximonosulfate (P2) or sodium perborate (P3). Tests were conducted on various materials using electrochemical tests (cyclic voltammetry, anodic potentiostatic transients, open-circuit potential (E) decay), Microscopic and Inductively Coupled Plasma (ICP) measurements. The results, when compared with those obtained on the same materials by using a conventional nitric acid paste (P1), indicate that the proposed pastes P2 and P3 are time stable, non toxic and as efficient as the P1 paste. Moreover, the protection of the tested SS can be further enhanced by adding small amounts of citric acid to, in particular, the P3 paste.

1. Introduction

One of the most important factors that determines the resistance of SS structures to pitting and crevice corrosion is the quality of the metal surface. Therefore, even if the high chromium content of SS makes it self-passivating upon exposure to air [1], any equipment whose surface has been altered by handling must undergo accurate cleaning (degreasing), pickling and passivating procedures to obtain a uniform passive layer.

The procedures reported in ASTM standard A380 recommend the use of warm nitric acid (from 20 to 70%, in the 49–71 °C temperature range for 30 min or from 10 to 15% at 66 °C for 4 h). There are, however, other patents, some of which have developed one-step processes for pickling and passivation [2–7]. But, in recent years, the ecological issues raised by these pickling and passivating processes have become increasingly important.

The aim of this paper is to formulate and analyse new passivating pastes that can provide a protective coating for SS surfaces against aggressive agents and, at the same time, decrease the chemical waste currently produced by nitric acid pastes [5–7]. The study was conducted using electrochemical techniques, (voltammetry, anodic potentiostatic transients, E decay), and by comparing the results from these tests to those obtained with the same materials oxidised by using a conventional nitric acid paste.

2. Experimental details

The materials tested in this work include commercial AISI 304L, AISI 316L, AISI 446 and SAF 2205 SSs of certified composition as reported in Table 1. The results obtained on AISI 304L SS are described in detail; the behaviour of the other examined SSs is reported by comparison. The disc-shaped samples had an exposed surface of 1 cm^2. The specimens were polished with fine grained emery paper (down to 1200), cleaned ultrasonically in acetone and then depassivated by cathodic reduction to remove the oxide film formed during previous treatment [8]. All the galvanostatic reduction curves (see Figure 4 and related comments) were carried out in deaerated (N_2) borate/boric acid (BB) solution (pH 8.4).

The specimens were then subjected to an oxidation through: (i) electrochemical anodization (in a deaerated (N_2) 0.1 M Li_2SO_4 solution at potential corresponding to the passivating zone: +400 mV vs SCE), (ii) by exposing them to the atmosphere for 24 h, or (iii) by treating them chemically with three kinds of passivating pastes composed as follows:

(a) Commercial HNO_3 paste (P1): HNO_3 60–70%, SiO_2 5–7%, surfactants 1–3%, commercial corrosion inhibitor 1–3%, H_2O balance.
(b) Oxone peroximonosulfate paste (P2): H_2SO_4 10%, Oxone peroximonosulfate 5%, SiO_2 5%, surfactants 3%, H_2O balance.

Table 1. Chemical composition (wt %) of AISI 304L, AISI 316L, AISI 446 and SAF 2205

Element	AISI 304L	AISI 316L	AISI 446	SAF 2205
C	0.018	0.017	0.18	0.011
Ni	9.15	10.52	–	5.52
Mn	1.75	2.0	0.81	1.55
Mo	0.36	2.10	–	2.92
Cr	18.1	16.8	26.5	22.11
S	0.016	0.03	0.003	0.001
P	0.028	0.045	0.19	–
Si	–	0.87	0.51	0.32
Fe	balance	balance	balance	balance

(c) Sodium perborate paste (P3): H_2SO_4 10%, $Na_2B_4O_7$ 5%, stabilizer 1%, SiO_2 5%, surfactants 3%, H_2O balance.

Before the voltammetric experiments, performed in deaerated (N_2) 10^{-3} M H_2SO_4 solutions, the chemically passivated specimens were washed in bidistilled water to remove the paste until no further acid reaction was detected.

The specimen, mounted on a Teflon electrode holder with the electrode contact made by an inner metal rod, was then transferred into a three electrode cell. After a cathodic polarization (30 s) at a potential near to that of zero current, the cyclic voltammetric curve started at a potential scan rate of 5 mV s^{-1}.

Electrochemical measurements were carried out using Amel (Italy) apparatus consisting of potentiostat, signal generator, interface, current integrator and differential electrometer. All the potential values are referred to the saturated calomel electrode (SCE).

In the potentiostatic current–time transients (carried out in deaerated (N_2) 10^{-3} M H_2SO_4 solutions), the anodic voltage step was preceded by specimen stabilization (60 s) at the corrosion potential (E_{corr}). The transients were carried out through the following procedure: after stabilization, the specimen was rapidly brought to the chosen potential and the current decay was then recorded over time.

The thickness of the oxide of the passive films was estimated by determining (using an inductive coupled plasma (ICP) technique), the amount of Fe, Cr and Ni in the solutions after the SS oxide dissolution in HNO_3 10% at 60 °C following a standard procedure [9]. The thickness of the oxide layer (around 3–4 nm) was calculated based on the hypothesis that all the oxides, after 2 h at 300 °C in a vacuum oven under Ar atmosphere, are present in the anhydrous form and by assuming a 5.2 g cm^{-3} average density of the passive film. After preliminary measurements on depassivated and passivated specimens, the appropriate immersion time was determined, assuring that a minimum amount of the oxide was always present on the surface and that the bare metal could be etched. This has been verified by voltammetric curves on the depassivated material. Thus, the calculated thickness of the oxide layer was presumably 10% lower than the actual value. This was verified by a X-ray photoelectron spectroscopy (XPS) determination performed on an electrochemical anodized specimen. However the calculated thickness is useful in comparing the different surface treatments.

3. Results and discussion

Figure 1 shows the voltammograms in deaerated (N_2) 10^{-3} M H_2SO_4 solutions carried out on AISI 304L specimens depassivated or passivated by applying the commercial paste P1 for 1 or 2 h [1]. It can be seen that, as the oxidation time increases, the decrease of the passivating current (i_p) is not appreciable.

The values of i_p obtained with the different materials after passivation in the atmosphere or by applying the commercial paste on the surface are reported in Table 2.

The passivation current decreases as the chromium content of the chemically passivated specimen increases and is practically unaffected by the presence of Mo when comparing AISI 304L (Mo 0.36 wt %) and AISI 316L (Mo 2.1 wt %), whereas it changes significantly by comparing AISI 446 (Mo 0 wt %) and SAF 2205 (Mo 2.9 wt %). i_p reaches the same value for AISI 316L, AISI 446 and SAF 2205 spontaneously passivated in the

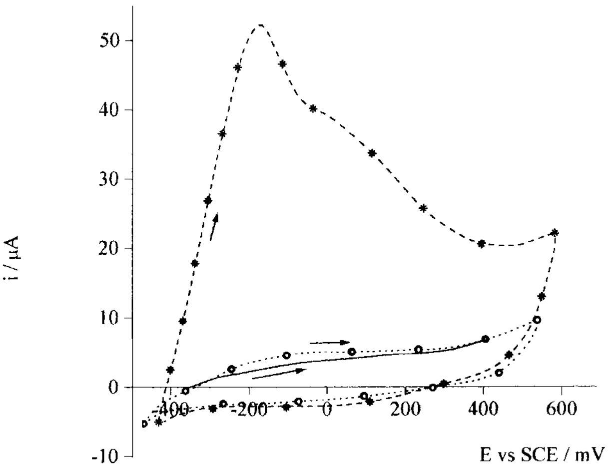

Fig. 1. Voltammograms obtained with AISI 304L specimens passivated with P1 (deaerated (N_2) 10^{-3} M H_2SO_4 solutions; scan rate: 5 mV s^{-1}; the arrow shows the scan direction). Reversal scan of test with P1 (2 h) was superimposed to the 1 h test. Key: (--∗--) depassivated specimen; (---o---) specimen passivated by P1 for 1 h; (——) specimen passivated by P1 for 2 h.

Table 2. Passivation current (i_p in µA cm^{-2}) obtained with different SSs passivated spontaneously or by P1 treatment

Specimens	Passivation current, i_p/µA cm^{-2} in deaerated (N_2) 10^{-3} M H_2SO_4			
	AISI 304L	AISI 316L	AISI 446	SAF 2205
Spontaneously passivated	41.6	20.3	20.5	20.3
Passivated by P1 (1 h)	5.1	5.0	4.1	2.0

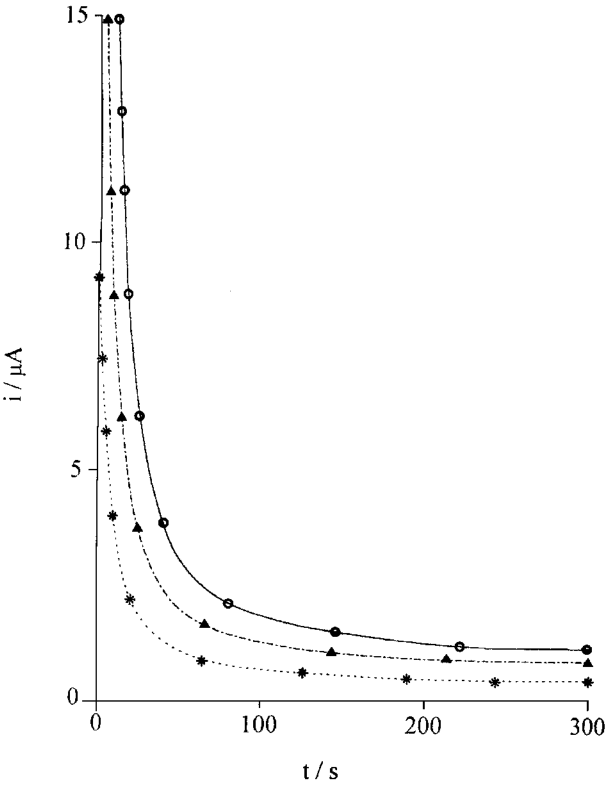

Fig. 2. Anodic transients obtained with depassivated and passivated (P1 30 min) AISI 316L specimens at +400 mV vs SCE (deaerated (N_2) 10^{-3} M H_2SO_4 solutions). Key: (- -∗- -) passivated with paste P1; (-·▲·-) passivated in the atmosphere; (—○—) depassivated.

atmosphere. Figure 2 shows the trend of the anodic potentiostatic transients performed with depassivated and passivated AISI 316L specimens [10, 11]. Figure 3 shows the transients obtained with passivated (P1 30 min) AISI 304L, AISI 316L and SAF 2205 specimens. The limiting passivation current is reached faster as the chromium content of the specimen increases.

The galvanostatic reduction curves, obtained in BB solution (pH 8.4) with AISI 304L specimens passivated 1 or 12 h, are shown in Figure 4. The change in slope of the curve ranging from +150 to −350 mV are correlated to the reduction of chromate, while those from −350 to −900 mV to the reduction of Fe_2O_3 [12].

As can be seen in Figure 4, the content of Fe_2O_3 in the oxide layer is low and decreases on increasing the contact time with the paste [13–15]. This may be ascribed to the transformation of Fe_2O_3 in Fe_3O_4, which is not visible at this solution pH [15]. The same behaviour was obtained when the specimens were passivated by the other pastes.

The variation of E over time for AISI 304L SS, measured in aerated or deaerated (N_2) 10^{-3} M H_2SO_4 solutions, is shown in Figure 5.

It is apparent that, while the potential of the specimen electrochemical anodized at +400 mV decreases slowly from +250 mV reaching a steady value in the passivity potential range, the potential of the chemically passivated specimens (P1 1 h) reaches a steady value in the prepassivation zone (E_{pp}) and then slowly shifts to more

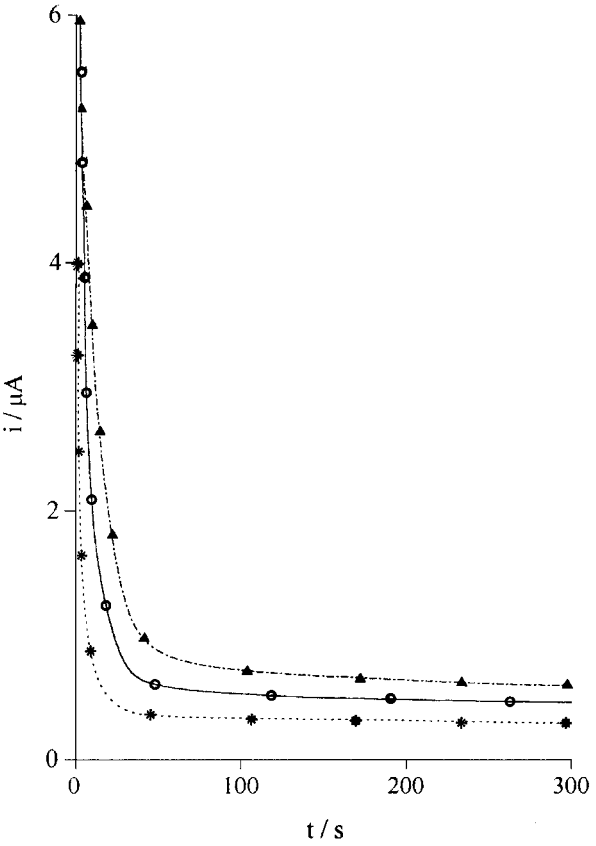

Fig. 3. Anodic transients obtained with passivated AISI 304L (▲), AISI 316L (○) and SAF 2205 (∗) specimens (P1 30 min) at +400 mV vs SCE (deaerated (N_2) 10^{-3} M H_2SO_4 solutions).

noble values, due to the presence of oxygen in the solution. In the deaerated (N_2) solution the potential reaches a stable steady value in the activity zone.

These results suggest that, because chromium oxide is insoluble in the medium used, its content in the chemically obtained passive layer should be lower than that produced by electrochemical anodisation. On the other hand, ICP measurements show that the Fe/Cr ratio, which in the electrochemically anodised specimens is about 0.5, increases to 4.3 in the oxide layer obtained after P1 treatment (Table 3).

Similar results were obtained with AISI 316L whereas chemically oxidised AISI 446 and SAF 2205 specimens behave like those that were electrochemically anodized. Furthermore, the time to reach the steady value in deaerated (N_2) solutions is linearly related to the chemical oxidation time when the paste application time is lower than 2 h (Figure 5).

Some authors report that in the *E*/*t* curves, before the rapid potential decrease, the time of the slow *E* decrease can be related to the oxide film thickness [16, 17]. By comparing the voltammetric results (Figure 1) with those of the *E*/*t* curves (Figure 5) it can be seen that, even if the value of the passivating current (i_p) after 1 and 2 h of contact with oxidizing paste is practically the same, the time of the slow *E* decrease (related to the oxide film thickness) results roughly doubled. The thickness of the passive film obtained with P1 treatment in

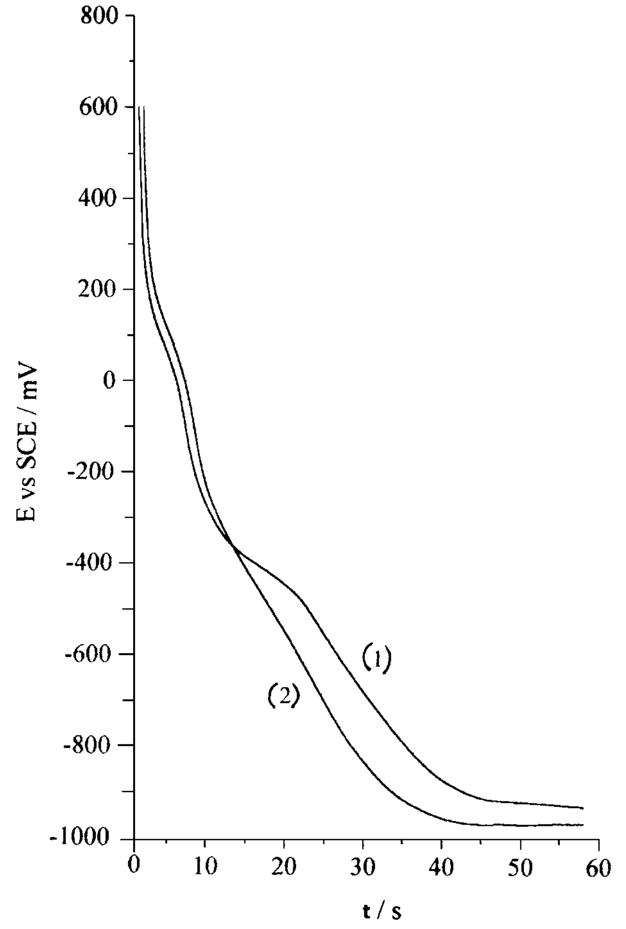

Fig. 4. Galvanostatic reduction curves obtained in BB solution (pH 8.4) with AISI 304L specimens passivated (P1) 1 h (curve 1) or 12 h (curve 2).

prolonged time tests (12 h) on AISI 304L specimens is around 3.3 nm (Table 3).

Table 3. ICP measurements on AISI 304L SS specimens

Type of treatment	Thickness of oxide layer/nm	Fe/Cr ratio
Chemically anodized	–	0.5
P1*	3.3	4.3
P2*	4.0	3.7
P3*	2.8	3.2
P3* + citric acid	4.1	3.0

*Time for P1, P2 and P3 treatments: 12 h

Figure 6 shows the voltammetric behaviour of AISI 304L specimens chemically passivated with the three different used pastes. In the 1 h tests, the lowest passivation current was obtained with the oxone peroximonosulfate paste (P2), but the best result was achieved with the sodium perborate paste (P3) after a prolonged application time (12 h). Nonetheless anodic potentiostatic transients carried out on the specimen passivated with P1 show a faster current decay and a value of i_p lower than that obtained after P2 treatment (Figure 7).

We have also verified that the time required to obtain a protective passivation is substantially reduced when the specimens are pickled in an HNO_3 pickling paste after the surface emery paper treatment [8, 18].

The change in E over time in aerated 10^{-3} M H_2SO_4 solutions is reported in Figure 8. This Figure also reveals the substantial effect obtained by adding 5% citric acid to the P3 paste.

As far as the time stability of the different pastes is concerned, Figure 9 shows the decrease in the persulphate and hydrogen peroxide percentages determined by sodium sulphite and potassium permanganate titrations [19]. Figure 9 depicts the degradation of the P2 paste which reaches a 70% stable activity after 120 days of storage, while the efficiency of the P3 paste linearly decreases with time, reaching a similar value after 150 days. After the paste is removed by rinsing with water, the specimen surface is smooth and, thus, both pastes seem suitable for SS passivation.

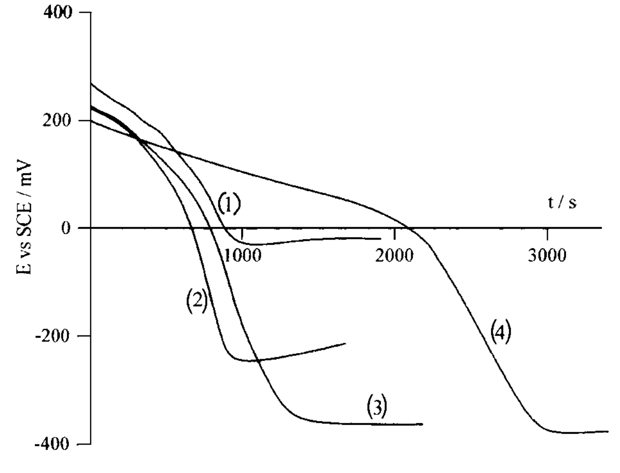

Fig. 5. AISI 304L SS open-circuit potential vs time (10^{-3} M H_2SO_4 solutions; curves 1 and 2: aerated solutions; curves 3 and 4: deaerated (N_2) solutions). After 1 h of electrochemical oxidation (curve 1); after 1 h of P1 treatment (curves 2 and 3); after 2 h of P1 treatment (curve 4).

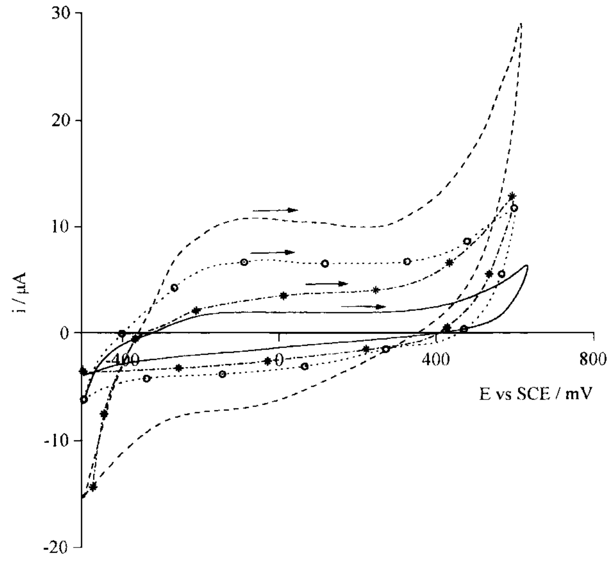

Fig. 6. Voltammograms obtained with AISI 304L specimens passivated with: (○) P1 (1 h), (∗) P2 (1 h), (- - - -) P3 (1 h) and (——) P3 (12 h) (deaerated (N_2) 10^{-3} M H_2SO_4 solutions; scan rate 5 mV s^{-1}).

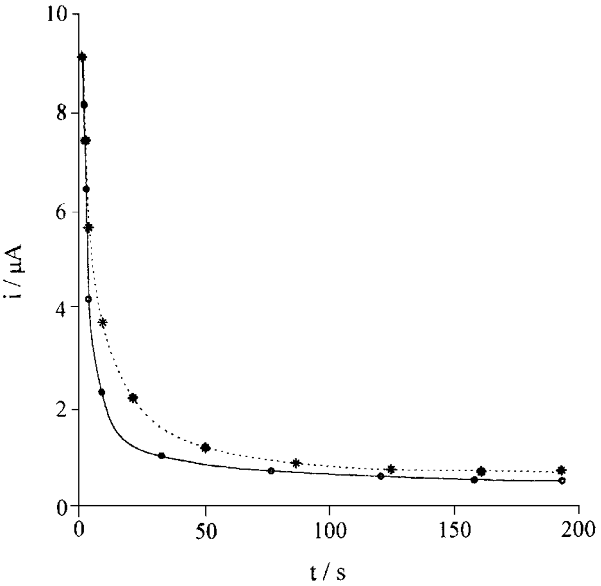

Fig. 7. Anodic potentiostatic transients obtained with AISI 304L SS passivated by P1 (—○—) or P2 (- -*- -) treatment (1 h) at +400 mV vs SCE (deaerated (N_2) 10^{-3} M H_2SO_4 solutions).

With regards to the chromium content in the oxide layer on the metal surface, the results in Table 3 indicate a significant decrease of the Fe/Cr ratio in the presence of citric acid. This effect could be due to a reaction of the acid with Cr^{3+} to give a citric acid Cr^{3+} complex avoiding its oxidation to soluble Cr^{6+} species.

Some tests also revealed that the surface treatments (cleaning, degreasing etc.) recommended before the application of the commercial paste cause the pitting attack, particularly when carbon impurities are present on the metal surface. This is especially prevalent in the welding zone and was confirmed when mild steel specimens were used. Thus, both the commercial and proposed passivating pastes cannot be applied to low alloy steels that can undergo serious corrosive attack.

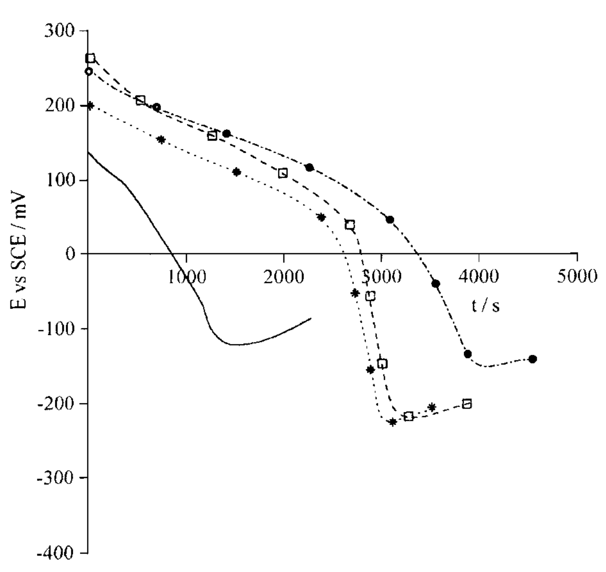

Fig. 8. AISI 304L SS open-circuit potential against time measured in aerated 10^{-3} M H_2SO_4 solutions, after prolonged treatment (12 h) by P1, P2, P3 and P3 + 5% citric acid. Key: (——) P3; (- -*- -) P1; (- -□- -) P2; (---o---) P3 with citric acid.

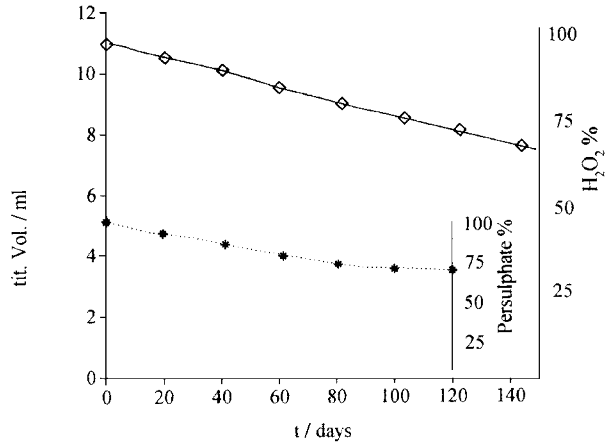

Fig. 9. Paste stability over time. Key: (—◇—) P2; (···*···) P3.

4. Conclusions

The following can now be stated:

(i) Pastes P2 and P3 provide protective steel coatings that are equally efficient as the commercial nitric acid paste (P1).
(ii) The proposed pastes P2 and P3 show no dissociation or degradation after lengthy storage and do not affect the metal surface by pit formation.
(iii) In comparison to the commercial paste, the new pastes decrease chemical waste and are nontoxic.
(iv) Surface chemical pickling prior to paste application significantly improves the effect of the paste.
(v) Carbon impurities have to be carefully eliminated from the welding zone because carbon causes discontinuities of the passivated metal surface.
(vi) The passivating pastes cannot be applied to low alloy steels which undergo serious corrosive attacks.

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