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THE EFFECT OF ALKALI AND SURFACTANT CONCENTRATION, TEMPERATURE AND STIRRING ON THE CLEANING EFFICIENCY OF THE CARBON STEEL SURFACE

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ABSTRACT Electrostatic painting is the fastest and most efficient technology through industrial paints due to its impact on the environment, and also for its very easy application on different surfaces. The first and most important stage of the electrostatic painting is to clean the surface to be painted by removing the dirt, lubricants, oils, metal oxides or welding residues. In order to increase the efficiency of carbon steel surface cleaning, the influence of alkali and surfactant concentrations, temperature and stirring was investigated. To produce a uniform surface required for the electrostatic painting, some degreased samples were subjected to pickling operation using aqueous HCl solution.

Keywords: *carbon-steel, degreasing, pickling, ultrasonication*

INTRODUCTION

A relatively new painting process, which is especially used in industrial or commercial applications, is electrostatic painting. This is the fastest and most efficient technology through industrial paints due to its impact on the environment,

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and also for its very facile application on different surfaces. At the same time, this type of painting can have a long warranty period compared to other painting methods. The electrostatic painting process is composed of several essential steps. The first stage is the chemical treatment which consists in removing dirt, lubricants, oils, metal oxides or welding residues from the part to be painted. Usually, these impurities come from mechanical processes of brushing or polishing. In the degreasing process, the organic pollutants due to mechanical or heat treatments are removed. In the pickling process, inorganic substances (rust, welding residues, stains, solid particles) are eliminated [1]. The degreasing efficiency depends both on the composition of the degreasing solution and the composition of the steel's pollutant. The degreasing mixture acts on the surface tension of the polluting particles and contains substances which facilitates emulsion, solubilization, flocculation and steel surface wetting action. The steel's pollutant are substances with polar groups that are absorbed onto the surface of the steel or by free fatty acids that form soaps adherent to the metal surface. In general, for chemical degreasing, a solution consisting of mild or strongly alkaline electrolyte, salt mixture and surfactants is used. The degree of electrolyte alkalinity depends on the sheet metal to be degreased. For degreasing steel and stainless steel, strong alkaline electrolyte is used. As a result of the chemical reaction between the alkaline substance and the oils and/or fats, these pollutants are removed by saponification. The salt mixture serves as a so-called builder substance and forms the basis of the solution. The surfactant lowers the surface tension and promotes, at a certain concentration, the formation of micellar solutions instead of molecular solutions [2-4]. The application of the degreasing mixture is done either by spraying or by immersion. The spraying application is used to eliminate large quantities of residues. In this case, the mixture is composed of alkali with silicates and phosphates. The immersion process involves introduction of the product in a high temperature alkaline solution. The high temperature reduces the viscosity of the impurities, increases the rate of chemical reactions. Therefore, the degreasing power is mainly due to the combined action of temperature, emulsifying power of the solution and mechanical or ultrasound agitation [5].

Agitation cleaning is ideal for hard metal objects that are placed on a moving platform. By moving the platform, the cleaning agent comes in contact with the bulk of the object and removes the contamination. Ultrasonic cleaning utilizes certain physical forces which occur when liquids are agitated by sound waves created by ultrasonic generators. The microscopic bubbles of vacuum created by ultrasonic stirring, form and collapse thousands of times each second. With each implosion, strong enough shockwaves to remove surface contamination are produced. The efficiency of ultrasonic stirring depends on the intensity of ultrasonic cavitation in the liquid, stirring time, temperature and chemical composition of the degreasing solution. The increase of temperature determines the decrease of the liquid viscosity and the amount of dissolved gas, which leads to increasing the cavitation intensity. The moderate increasing of the liquid temperature brings it closer to its vapor pressure, and so the most effective form of cavitation, in which the cavitation bubbles are filled with the vapor of the cavitating liquid, is achieved. The optimum temperature for the most highly caustic cleaners is between 80-90^{o}C, the chemical effect being strongly enhanced at this temperature.

The current paper investigates the effect of alkali (PRESOL 7120, 6-90g/l) and surfactant (AB40, 2.5 to 10 ml/l) concentration, temperature (50 to 70^{o}C) and stirring type (magnetic or ultrasonic) and time (5 to 15 min) on the degreasing/ pickling efficiency of the carbon steel (S235 plate). To produce a uniform surface characteristic required for the electrostatic painting, some chosen degreased samples were subjected to pickling operation for 15 min using 15% aqueous HCl solution.

EXPERIMENTAL

Materials and Methods

To evaluate the influence of different parameters on the degreasing / pickling efficiency, samples of carbon steel plate S235 (C% - max 0.22; Mn% - max 1.60; S% - max 0.05; P% - max 0.05; Si% - max 0.05) from CAN STEEL PRODUCTION SRL, having dimensions (20x10x1) mm, are used. The steel samples were clamped to a support placed on the edge of the Berzelius cup (V-150ml) so that the entire sample surface was immersed in the degreasing solution. After each degreasing / pickling operation, the samples were three times washed with distilled water and then dried with hot air.

To prepare the degreasing electrolyte PRESOL 7120 was used (COVENTYA S.A.S, 92588 CLICHY CEDEX – FRANCE) consisting of sodium hydroxide (50-100%) and disodium metasilicate (10-25%) which was dissolved in distilled water. The Presol concentration was varied between 6 and 90 g/l.

Surfactant AB 40 consisting of C12-14 alcohols (ethoxylated and sodium sulphates salts) 25-50%, non-ionic surfactant < 2.5%, sodium dodecylbenzene sulphonate 10-25% and phosphoric acid < 2.5% was used for adjusting the surface tension of the degreasing electrolyte. Its concentration ranged from 2.5 to 10 ml per liter of degreasing electrolyte. To prepare the 15% aqueous HCl solution used at pickling operation it was used HCl 37% from Sigma-Aldrich.

For stirring of the degreasing electrolyte, a magnetic stirrer MSH-20D (WITEG LABORTECHNIK GmbH, Wertheim Germany) provided with a heating system and temperature sensor, respectively, an ultrasonic cleaner (ultrasound power- 60W, volume 1.3L) equipped with temperature and duration control system, produced by ISOLAB LABORGERÄTE GmbH, Germany was used. The Presol concentration was determined by titration with 1N HCl in the presence of the phenolphthalein until that a colour change from violet to colourless was observed. Concentration of degreaser in the bath was calculated using the formula: C_{Presol} (g/l) = $V_{ml\ of\ HCl}$ x 5.56.

The surface tension of degreasing solutions was measured using the drop volume method and the formula:

$$\sigma = \sigma' \cdot \frac{n'}{n} \cdot \frac{\rho}{\rho'}, \qquad (1)$$

where σ', n' and ρ' represent surface tension, drop number and density for distilled water, while n and ρ represent the number of drops and density, respectively, for degreasing solution [6]. The degreasing efficiency was followed by scanning electron microscopy-energy-dispersive X-ray (SEM-EDX) using a Hitachi SU8230 scanning electron microscope, at an electron acceleration of 30kV, obtaining images between 30x to 50,000x magnification. The samples were sectioned to the size of 0.5 / 0.5 cm, using a diamond disk with the Micracut 151 device. Then, the samples were fixed on brass supports (stabs) of the microscope with the help of double-sided carbon sticks from Agar Scientific with a diameter of 12 mm and with silver paste also from Agar Scientific. For all samples, images were taken at identical magnifications: 30x, 100x, 500x, 1000x, 5000x, 10,000x, 20,000x, 50,000x. EDX (Energy-dispersive X-ray spectroscopy) analyses were performed using AZtech software from Oxford Instruments, obtaining at least two spectra per sample. A mapping analysis of the distribution of chemical elements in the sample was also performed.

RESULTS AND DISCUSSION

As it can be seen from **Fig.1 A**, the surface tension decreases with the increasing surfactant concentration. In the logarithmic representation of the surface tension as a function of the surfactant concentration there are two linear regimes, namely below and above the critical micelle concentration (CMC) (see **Fig. 1B**). The common procedure to determine the CMC from experimental data is to look for the intersection of two straight lines traced through plots of the measured property versus the surfactant concentration. The CMC is the surfactant concentration from which the micelles are formed. Above the CMC, the interfacial surfactant concentration does not change any more and the surface tension of the solution is practically constant.

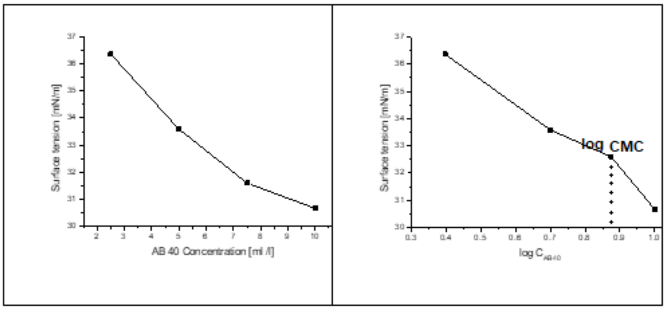

Fig. 1. Surface tension of the AB 40 aqueous solution for different concentration of surfactant (**A**) and surface tension vs. logarithm of AB 40 concentration (**B**). The errors were found to be of maximum 5% of the measured values.

In **Fig. 2** it can be seen that the value of the surface tension increases with increasing of the Presol concentration.

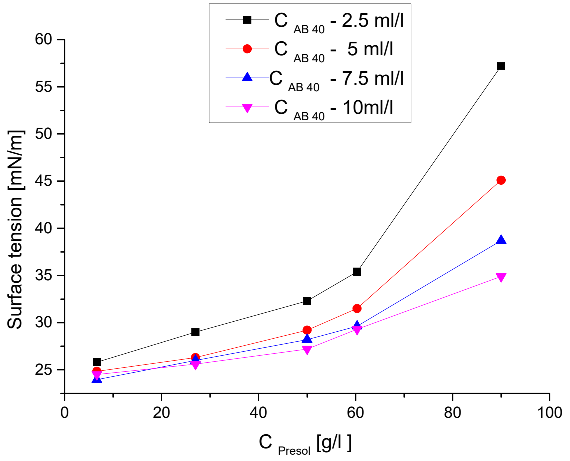

Fig. 2. Surface tension of the degreasing solution vs. Presol 7120 concentration at different AB 40 surfactant concentrations

This means that Presol is tensioinactive, its concentration being lower in the surface layer than inside of the liquid phase. However, it can be observed that as the surfactant concentration increases from 2.5 to 10ml/l, the surface tension decreases. This decreasing surface tension is due to the fact that in the surface layer the concentration of the dissolved substances is larger than inside the liquid phase, so the molecules dissolved are adsorbed at the interface.

In the graphical representation of the surface tension vs. AB 40 concentration (see **Fig.3**) it can be observed that as the Presol concentration increases, the change of slope takes place at increasing values of surfactant concentration. This means that the increase of the Presol concentration, in the degreasing solution, leads to delay in the onset of micelle formation, respectively to the increase of the critical micellar concentration of the AB 40 surfactant (see **Table 1**).

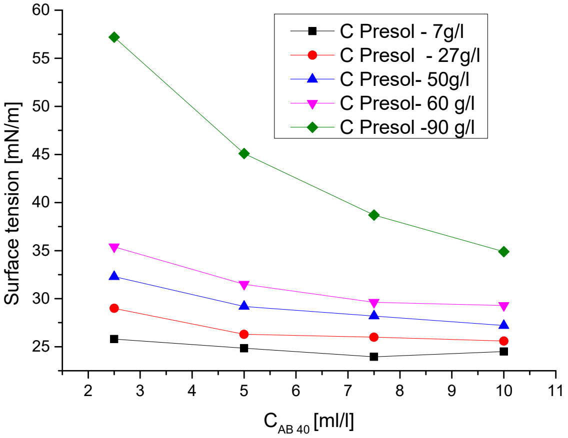

Fig. 3. Surface tension of the degreasing solution vs. AB 40 surfactant concentration at different Presol 7120 concentrations

In the degreasing process, the formation of micelles is desirable and therefore the knowledge of the CMC is very important. Critical micellar concentration specifies the limiting concentration for meaningful use and it is a measure of the efficiency of a surfactant.

Table 1. Critic micellar concentration of the surfactant AB 40 at different Presol concentration

C_{Presol} [g/l]	log CMC	$CMC_{AB\ 40}$ [ml/l]
0	0.875	7.5
7	0.699	5
27	0.699	5
50	0.699 - 0.875	5 - 7.5
60	0.875	7.5
90	>1	>10

In the **Figs. 4 and 5** the SEM images, and the elemental composition determined by EDX of the carbon steel sample, before and after degreasing operation, are showed.

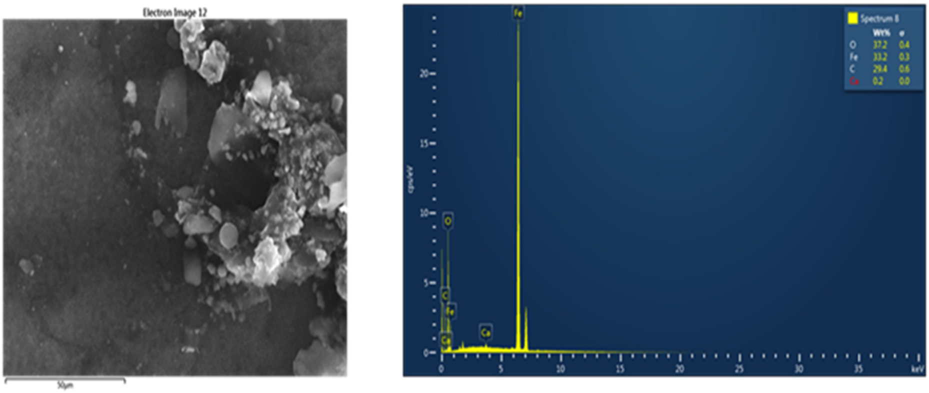

Fig. 4. Selected SEM image of the non-degreased carbon steel sample and its elemental composition determined by EDX

The experiments performed under different stirring speeds highlighted the beneficial effect of electrolyte agitation on the cleaning process of the sample. As can be seen from **Fig. 6**, after 15 minutes of degreasing of the carbon steel sample at temperature of 60^{O}C, in a solution containing 50 g/l Presol and 7.5 ml/l AB 40, the percentage of carbon determined by EDX analysis, decreases from 29.9 to 17.8 and respectively from 29.9 to 14.3% with increasing agitation speed from 400 to 800rpm.

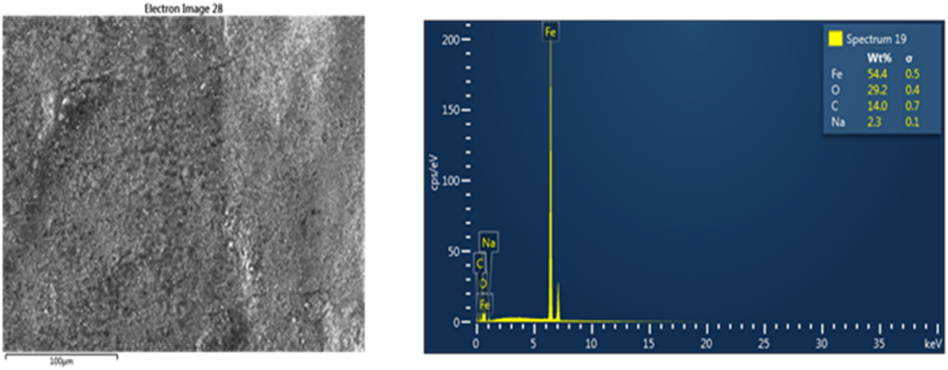

Fig. 5. Selected SEM image of the carbon steel sample degreased in the electrolyte containing 50g/l Presol and 10ml/l AB 40, at 70^{0}C, 600rpm, 5min and its elemental composition determined by EDX

As the cleaning solution dissolves the surface contaminant, a saturated layer develops at the interface between the fresh cleaning solution and the contaminant.

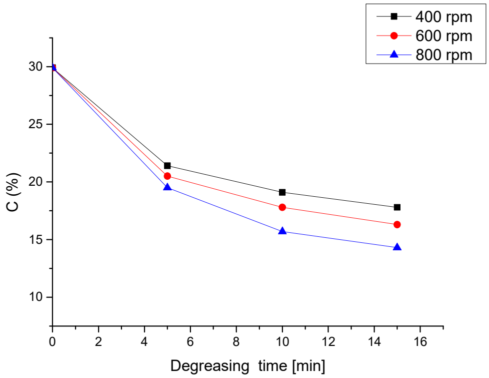

Fig. 6. Decreasing the percentage of carbon vs. degreasing time using a solution with 50 g/l Presol and 7.5 ml/l AB 40 at different stirring speeds and temperature of 60^{O}C

Saturated solution can no longer attack the contaminant and therefore the cleaning action stops. By increasing of the stirring, a fresh degreasing solution can reach easier the contaminant. Increasing the temperature of the degreasing electrolyte from 50 to 70^{0}C favors the removal of organic pollutants from the surface of the carbon steel sample, the percentage of carbon decreasing from 8.5 to 5.3% at 50^{0}C and respectively from 8.5 to 3.2 % at 70^{0}C (see fig.7). Higher temperatures decrease the contaminants viscosity, and increase the diffusion of the degreasing solution to the steel surface, allowing easier contaminant removal. Increasing the Presol concentration from 30 to 90g/l leads to decrease of the carbon concentration from 14.2 to 1.8% after 15 min of degreasing at 70^{0}C and a stirring speed at 800rpm (see fig.8). Increasing the Presol concentration, increase the NaOH concentration which converts, by saponification, the natural fats, i.e., esters of glycerol and higher fatty acids, into glycerol and the sodium salt. These substances are water soluble and are easy removed by rinsing. The mineral fats (oils) are not decomposed by alkalis but are dispersed and suspended in alkaline solutions through an emulsification process. As the increase of the Presol concentration also increases the concentration of the sodium metasilicate (present in Presol degreaser along with NaOH). This being an excellent emulsifying and suspending agent the increase of its concentration determines the improvement of the degreasing efficiency [7].

To dissolve iron oxides from the surface of carbon steel sample and to clean light rust without any significant attack on the steel itself, the HCl acid pickling was used. HCl pickling has the advantages of lower costs, lower acid consumption and greater utilization of the acid, greater versatility and more uniform product quality than sulfuric acid pickling. Pickling rate increases as acid concentration and for this reason an acid solution with a concentration of 15% HCl was used.

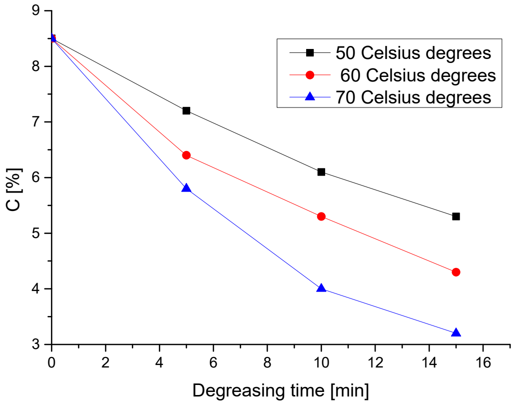

Fig. 7. Decreasing of the percentage of carbon vs. degreasing time using a solution with 50 g / l Presol and 7.5 ml / l AB 40 at a stirring speed of 600rpm

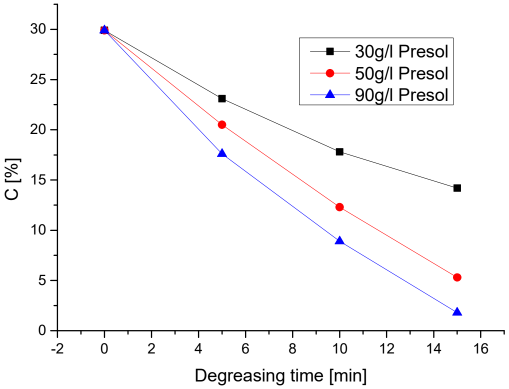

Fig. 8. Decreasing of the percentage of carbon vs. degreasing time at temperature of 70^{0}C using a solution with different concentration of Presol, an AB 40 concentration of 7.5 ml/l and a stirring speed of 800rpm

As it can be seen from **Fig. 9**, after 15 min of HCl pickling at room temperature, the oxygen concentration of the degreased sample decreased from ~37 to ~5%. Practically, the acid dissolves the iron oxides presence on the steel surface according to the following reaction mechanism:

$$Fe_2O_3 + Fe + 6HCl = > 3\,FeCl_2 + 3H_2O$$
$$Fe_3O_4 + Fe + 8HCl = > 4FeCl_2 + 4H_2O$$
$$FeO + 2HCl = > FeCl_2 + H_2O$$

By iron oxides elimination, the HCl pickling permits proper adherence of a subsequent metallic coatings and promotes surface smoothness of the finished product.

As it can be seen from **Fig. 10**, the pickling operation can be avoided by using steel degreasing in the presence of ultrasound. It is observed that by degreasing in the presence of ultrasound for 5 min, the iron oxides are practically removed from the surface of the steel sample. The effect of ultrasonication is consistent with the micro-agitation helping both the dissolution of soluble contaminants and the removal of insoluble particles. Ultrasonic activity enhances also the effect of many chemical reactions by high pressures and temperatures created at the implosion sites. Ultrasonic cavitation and implosion effectively displace the saturated layer on the steel surface to allow fresh degreasing solution to come into contact with the contaminant remaining to be removed [8].

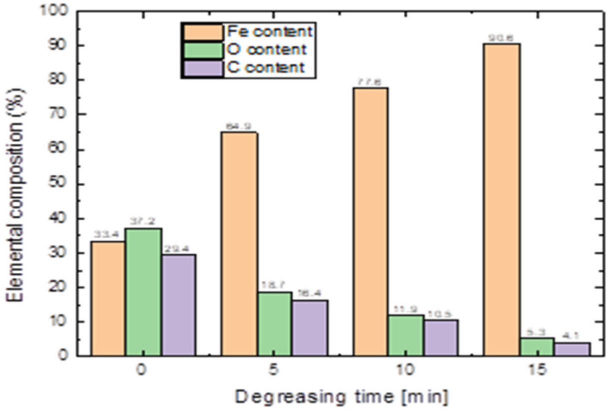

Fig. 9. Elemental composition of the carbon steel samples degreased at 70^{0}C and magnetic stirred (600rpm) with an aqueous solution containing 50g/l Presol and 7.5 ml/l AB 40, and then pickled in 15 % hydrochloric acid for 15 min, the stirring speed being 400rpm

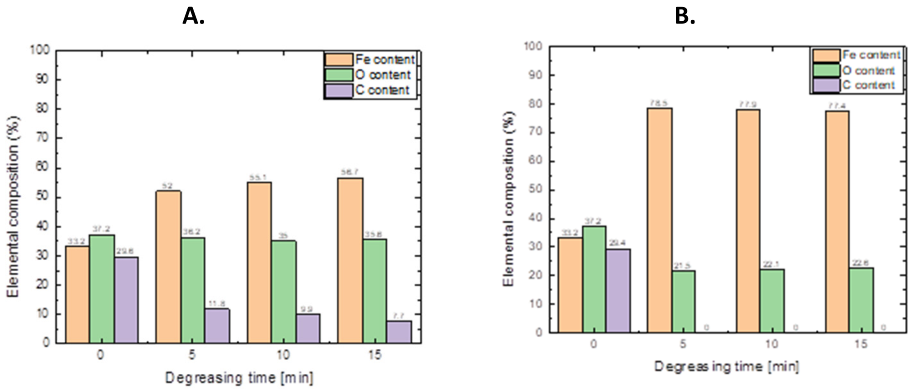

Fig. 10. Elemental composition of the carbon steel samples vs. degreasing time at 70^{0}C, in an aqueous solution containing 50g/l Presol and 7.5 ml/l AB 40 using magnetic stirrer (600rpm) (**A**) or performing degreasing in the presence of ultrasound (**B**)

Properly utilized, ultrasonics is a technology of today, the ultrasonic energy contributes significantly to the speed and effectiveness of immersion cleaning processes.

CONCLUSIONS

Increase of the Presol concentration leads to delay in the onset of micelle formation, respectively to the increase of the critical micellar concentration of the AB 40 surfactant. The AB 40 concentration must be at least 7.5ml/l for Presol concentration greater than 50g/l.

With Presol concentration and electrolyte temperature increasing, from 50 to 90g/l, and respectively from 50 to 70^{0}C, the efficiency of the steel surface cleaning process has improved.

To dissolve iron oxides from the surface of carbon steel sample and to clean light rust without any significant attack on the steel itself the HCl acid pickling can be used after the degreasing stage or performing degreasing in the presence ultrasound.

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