Problems of blackening of steel parts in technical practice

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Abstract. Problems of degradation are mainly solved in finished products, in a number of cases it is manifested during production. A great influence on the degradation processes of the products has the surface quality and surface finish. The article deals with the problem of blackening of steel, which has been treated with alkaline blackening. The throttle shaft made of automatic steel will be analyzed. Degradation was manifested by a change in surface quality after alkaline blackening. The methods of light and electron microscopy in combination with complex analysis of production flow and technology conditions were used for analysis. Based on the results of analyzes it was found that the degradation processes are closely related to the quality of preparation of the surface. Owing to the incorrect pretreatment of the surface, oxides occurred locally. At the sites of oxides, after alkaline blackening, the surface layer was peeled off, resulting in deterioration in the quality of the product.

Keywords: Degradation, Blackening, Steel, EDX analysis

1 Introduction

Degradation is primarily known as a manifestation of environmental influences or degradation of material properties for already finished products. However, degradation may already occur in the component manufacturing process. Significant influence on degradation processes has the effect of surface quality and surface treatment.

The surface properties depend on the surface structure, the chemical, physical, mechanical and geometric properties of the surface layer [1-3]. The free surface structure forms the surface of a large set of grains, which forms the interface between the solid phase and the surroundings. A characteristic feature of the surface is a step change in the symmetry of forces acting on the atomic nuclei of the crystal lattice. Within the volume forces are compensated in different directions, while on surface they are not compensated [4,5].

Under chemical properties we mean changes in chemical composition or oxidation states at the interfacial interface. On the surface, in contact with the liquid medium, a combination of anodic oxidation (metal dissolution) and cathodic reduction (oxygen reduction or hydrogen excretion) can take place. The dissolution of the metals can take place in two ways.

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Reviewers: Karol Vasilko, Dana Stančková

The first method is active dissolution where the surface is not coated with any protective film. The second option is passive dissolution, when insoluble compounds are formed on the surface [4].

Many methods are used to improve surface quality. They may be mechanical, chemical, electrochemical, thermal and chemical-thermal treatments. The purpose of the surface treatments is to obtain a higher corrosion resistance of the product, to achieve the desired appearance or to improve the mechanical properties of the surface. It is mainly used as a finishing operation [6-8].

All surface treatments, other than mechanical, are based on the formation of a layer on the base material that meets the required properties.

This article focuses on the blackening of steel parts. Alkaline blackening is a coating that is the most common way to dye steel products, and above all to ensure improved appearance of the part being treated. Its purpose, combined with preservatives, is also an increase in corrosion resistance. The result of alkaline blackening is the formation of a conversion oxide layer of about 1 μm thick. The principle of alkaline oxidation blackening consists in iron oxidation by immersion of ferrous metal products into a concentrated hot aqueous solution of a mixture of sodium hydroxide with a suitable oxidant and other ingredients added to the bath. These are inorganic or organic chemicals, called accelerators, inhibitors, wetting agents, complexation agents and others [9-11].

The process itself takes place in several steps (Fig. 1). First, degreasing parts and rinses will result in the removal of dirt from the surface of the component (dirt, oil residues after pre-treatment). If any residual grease remains on the surface of the component, stains will form on the surface. Subsequently, alkaline blackening is performed in the first bath, followed by cascade washing. In most cases, two-stage blackening is performed to ensure a uniform layer across the entire surface of the part, so the last two steps are done again. After the second blackening, the parts are rinsed with hot water to ensure that the scrubbing residue does not enter the preservation bath. After rinsing, the components are preserved to ensure corrosion resistance.

Fig. 1. Blackening process

The quality of the resulting surface layer depends on several factors. One of them is the quality of pre-fabrication of the component. It is very important that the products are well degreased and that there are no impurities on them to prevent the formation of the surface layer. Another factor is the temperature of the bathing bath. The calcination takes place at a boiling point of the sodium hydroxide solution, which is approximately 140 °C. At this temperature there is a considerable evaporation of water. By reducing the water content the concentration of the bath changes and thus the boiling point changes. Therefore, it is necessary to constantly monitor the temperature of the scrubbing bath and to check the quality

of the preparation, e.g. adding water or adding individual components of the scrubbing agent (NaOH and oxidizers) [10].

As with any process, even with alkaline blackening, defects occur. Some can be repaired, for example, by re-blackening, but some can be not been repaired. It may be small black layer thickness, uneven layer thickness, brown spots on the surface or corrosion.

The aim of this paper is to analyze the causes of the specific defects that arise on surface-treated components and this is alkaline blackening. The component being analyzed will be a throttle shaft that affects the amount of intake air into the engine.

2 Description of the problem

The parts were made of standard automatic steel 11SMnPb30 according to CSN EN 10027-1. For the production of these components are used chip machining technologies mainly turning, milling and grinding. Part of these products are further processed by surface treatment - alkaline blackening. Each of the technologies used, the manual operations carried out between the various machine operations (e.g. dimension checks), not least storage, bring a number of risk factors. These factors are reflected in defective products. These may be defects in size, shape, appearance, or corrosion. The defect, which is dealt with in this article is manifested by the occurrence of colour spots on the surface of the component and its cavities. There are more manifestations of this defect. The first signs are colour spots on the cylindrical surface or in the threaded hole. Another manifestation is the presence of impurities or sediments in holes components.

Factors that affect quality can be divided into internal and external. Among the internal factors we can include the chemical composition of the material (content of harmful, alloying elements), the material structure (grain size, pores size), inclusions (type, distribution, size and shape), internal stresses in the entire crosssection and surface layers, material (roughness, surface hardening, etc.). Among the external factors we can include the influence of environment (temperature, humidity during storage, transport and production), used technology (type, used parameters), used tool (material, geometry, quality, wear), cutting fluid (composition, age, temperature) Washing and drying (temperature, bath concentration, soaking time, drying temperature, drying time), blackening (grease residues on components, concentration of dirt, surface roughness, blackout, bath temperature), manipulation, human factor.

Fig. 2. Stains above the hole

Fig. 3. Deposits in the hole

3 Analysis of causes of part degradation

Stain and sediment analysis was performed visually and using the Tescan Vega 3 electron microscope.

Stains appeared near the flap holes. These are irregular shapes that have a partially white (Fig. 4a) and a partially red colour (Fig. 4b).

Fig. 4. Stain at hole.

From an electron microscope observation, it is clear that on the surface of the material the oxide is present (Figure 5). This shows on the presence of oxides on the surface of the component before the blackening process. Oxides on the surface were probably due to improper pre-treatment of the surface before the blackening process.

Due to the presence of oxides on the surface of the component, the protective layer, formed during the blackening process, has not been bonded to the base material. Subsequently, the black layer was peeled off. The surface of the material is highly cracked after peeling.

Fig. 5. Layer of oxides, REM

A surface was conducted EDX analysis to determine the orientation chemical composition in and outside areas the presence of oxides. The results (Tab. 1) show that in the areas where the surface layer has peeled, the oxygen content is much lower. In addition, there are other differences in the chemical composition of selected analysed areas.

The greatest differences between the results of surface EDX analysis in the non-oxide region (Figure 6a) and the oxide regions (Fig. 6b) are in Fe, O and C. The increased oxygen content is due to the formation of iron oxides on the surface of the component. Increased content C (approx. 4 x) may be due to imperfect degreasing. Interesting is also Na content. Although blackening occurs in sodium hydroxide solution, and the rinses are carried out in sodium hydroxide solutions, no Na content was found.

Table 1. Results of area EDX analysis [wt%]

Area	Fe	C	Mn	S	Mo	Pb	Bi	Si	O	Cu	Na	Ca
a	74.86	13.76	13.49	0.09	6.52	0.23	0.47	0.12	0.00	0.03	0.00	0.02
b	34.45	15.50	17.85	0.28	4.31	0.99	1.41	0.00	34.57	0.11	0.00	0.02

Fig. 6. Analyzed areas, area EDX analysis

In addition, analyzes were carried out to determine the causes of the formation of sediments (Fig. 3) in the holes of the part. It was supposed to be the sediment of the foam produced during the blackening process. Incorrectly set conditions in the scrubbing bath can result in foam formation. This foam was then blown into the holes in the component and did not eliminate the washing of parts. Subsequently, in the drying process, the foam crystallized (Fig. 7). This assumption confirmed electron microscope observation. Detailed observations show a crystalline sediment structure. Furthermore, it can be seen that crystallization proceeded at different speeds (Fig. 8).

Fig. 7. Sediments in the hole, REM

Fig. 8. Sediments, detail, REM

Surface EDX sediment analysis also confirmed that it is a scouring bath residue (Tab. 2). It is predominantly a mixture based on iron oxides.

Table 2. Results of area EDX analysis [wt%]

Sample	Fe	C	Mn	S	Mo	Pb	Bi	Si	O	Cu	Na	Ca
Sediments	25.94	9.35	4.08	0.00	3.70	0.11	0.20	0.00	56.22	0.00	0.20	0.00

3 Conclusions

The aim of the paper was to show the problem of blackening of steel parts in technical practice, which has to solve the occurrence of defects on the components, which have been treated with alkaline blackening. Specifically, it was a throttle shaft, where it was important to analyze the cause of the defects and remove this cause.

On the basis of an assessment of internal and external factors, it was assumed that degradation could in the first case have been caused by incorrect pre-treatment of the surface before the blackening process. In the second case the suspected impurities in the holes of the parts.

Based on the results of electron microscopy, it can be stated that in the first case the products were not sufficiently degreased and subsequently passivated. This has resulted in the formation of oxides during storage and transport. Oxides at the surface of the component caused a weakening of the adhesion of the subsequent surface treatment. Due to the reduced adhesion, the surface layer was peeled off. One way to reduce this defect is by introducing the pickling of the components before the blackening process. In the second case the cause is the uncorrected prepared blackening process. By blackening form the foam on the surface of the tank. This foam was then blown into the holes in the components. The washing process did not remove it and the foam crystallized.

This paper confirms that in the surface treatment technologies, which consist of several stages, it is important to follow the prescribed conditions and procedures for each of the intermediate steps. This is the only way to assure the required quality and durability of the manufactured part.

Authors are grateful for the support of grant No. CZ.1.05/4.1.00/11.0260 EDIMARE and SGS FME JEPu in Ústí nad Labem for 2018.

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