Carbon steel carabiners improvements for use in potentially explosive atmospheres

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Abstract. In cases where an explosive atmosphere contains several types of inflammable and/or combustible gases, steams or powders, the protection measures must be appropriate to the highest possible danger. However, the employer must pay special attention to the workplace and to any factor that can influence the working conditions, especially to those related to the workers. Therefore, any device, tool or equipment used by the human operator must possess special properties. In addition to protective clothing, workers who work at heights must receive personal protective equipment against falling that includes multiple linking elements known as carabiners. The carabiners used in this equipment must be made of non-sparking material. The aim of this paper is to propose a spark characteristic improvement of carbon steel used in carabiners manufacturing by deposition of zinc phosphate coating.

1 Introduction

Explosion prevention and explosion protection are of major importance to workers safety and health, as explosions endanger human life and health as a result of the uncontrolled flame effects and pressure (projected particles), the presence of toxic products and oxygen consumption in the air they inspire. In addition to this, material damage can be significant.

The European Directive ATEX 2014/34/EU regulates the conditions for the use of electrical and non-electrical equipment in potentially explosive areas [1].

Potentially explosive atmosphere means an atmosphere that can become explosive due to local or operational conditions. This occurs as a result of a mixture of air with gases, dust, fumes or other flammable substances. If this flammable mixture comes into contact with a source of ignition (spark) then the explosion is triggered. In order to prevent an explosion, workers receive personal protective equipment which must correspond to the requirements for their use in explosive atmospheres[2, 3].

The prevention of ignition hazards must take into account electrostatic discharges, where workers or the working environment act as carriers/producers of electrical charge.

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Therefore, any item of clothing or personal protective equipment must be made of materials that do not produce electrostatic discharges which can lead to the ignition of the explosive atmosphere [1].

In some hazardous areas, depending on the probability of triggering an explosion, the surfaces of the insulating material are delimited.

The installation, equipment, protection systems, and all the connecting devices must be made of materials that prevent or reduce the risk of an explosion.

The ATEX Directive specifies that any personal protective equipment which will be used in an area with potentially explosive atmospheres must be made of materials which cannot be the source of electric or electrostatic springs, impact springs or sparks [1].

In areas where technical and organizational measures do not provide adequate protection, according to the Occupational Safety and Health Act 319/2016, the employer must provide personal protective equipment to the worker [4, 5]. This equipment must be appropriate to the risk to which the worker is exposed and do not endanger his health or life. Moreover, the worker must know how to use the personal protective equipment and keep it in optimal conditions of use [6-8].

The personal protective equipment is given to the worker following a risk assessment when he is exposed to risk factors (physical, mechanical, chemical etc.), based on a grant sheet of personal protective equipment [9, 10].

The carabiners are components of the safety systems used by the worker in order to prevent falling from a height. These are generally made of aluminum alloys and steel [11].

When tensile strength and high-temperature resistance are important factors in choosing a carabiner, steel carabiners are used. Typically, they are made of carbon steel due to its high strength properties and low price [11].

When the carbon steel carabiners are used in the mine, they must possess good corrosion resistance and high anti-spark properties. In order to improve these properties, a layer of insoluble zinc phosphates can be deposited on the surface of the body of the carabiner (Figure 1).

Fig. 1. The main carabiners components/ the carabiner body

Through this method, a non-electrical conductive layer can be obtained on a steel surface which will protect the carabiner against electrostatic discharges [12]. This

homogeneous layer will also significantly increase the material corrosion resistance in harsh mine environmental condition [13].

2 The phosphating process

The phosphating process can be defined as the formation of an insoluble phosphate layer on the metal surface by a chemical reaction which occurs between its surface and the phosphate solution. In case of this type of coating, in addition to increasing the corrosion and the surface electrical resistance properties, the phosphate layer not only covers the entire surface of the material but also bonds with the base material. Moreover, the phosphate surface presents excellent characteristics for further coating with lubricating solutions or mechanical shock absorbent layers, such as rubber-based paints [15, 16].

The phosphating process consists of multiple stages which are presented in Figure 2. Depending on the surface properties on which the phosphate layer will be deposited, and depending on the substances used to make the solutions, some steps can be added or removed. After every phosphating stage, the samples rinsing is recommended in order to remove the soluble active salts which remain on the deposited layer surface [17].

Fig. 2. The stages of the phosphating process

One of the main stages of carabiner manufacturing is the metal surface cleaning after modeling. This one can also be used as a stage of preparation of the carabiner surface for the phosphating process. However, because the structure and the type of the metal surface can have negative or positive influences on the phosphate layer, the carabiner's body surface can be cleaned and activated by grinding and polishing or by sandblasting with ceramic particles.

In order to obtain a phosphate layer with the above-mentioned properties, the deposition surface must be prepared by chemical methods. Therefore, prior immersion in the phosphating solution, the sample must pass through two previous stages, named chemical alkaline degreasing and pickling. After each stage, the carabiners should be rinsed in water for the removal of the chemical compounds on the surface of the surface, which results from degreasing and pickling. The final stage of the phosphating process, drying, could be performed at room temperature or at slightly high temperatures by means of drying stoves [17, 18].

2.1 The alkaline degreasing

It is well known that carbon steel has low corrosion resistance, so it oxidizes when it is stored in places where the atmosphere present humidity. Usually, in order to prevent the atmospheric oxidation, the steel is covered with a thin layer of oil or grease.

Before being phosphate, the carbon steel surface must be free of greasy particles in order to obtain a homogenous surface covering. A greasy surface can lead to uneven pickling, therefore, only a part of the surface will be activated. Steel degreasing must be performed especially for the removal of oils or greases used during the production of the material and for the disposal of other residues [19]. The optimal period of time for the degreasing stage depends on the level of contamination of the sample surface and can be visually checked by lifting the sample from the degreasing solution at regular intervals. Another important factor in this stage is the solution temperature. In this study, the

carabiners have been immersed in the degreasing solution for 10 minutes at an 85 °C solution temperature.

The chemical composition of the alkaline degreasing solution used to clean the surface of the carabiner body, as well as the amount of the compounds for 2 liters of solution, are shown in Table 1. All the compounds have been dissolved in distilled water.

Table 1. Chemical composition of degreasing solution

Compound	Sodium hydroxide [g]	Sodium carbonate [g]	Trisodium phosphate [g]	Sodium silicate [g]	Surfactant [g]
Amount	90	60	60	10	13

Sodium hydroxide is used in the manufacture of soap, therefore is one of the main substances used in degreasing solutions. It, also called caustic soda, is a white alkali caustic base that can decompose the proteins at ambient temperature, the chemical formula being NaOH [19].

Sodium hydroxide absorbs moisture and carbon dioxide from the air, making it very soluble in water. In our case, like the other substances used, the amount of sodium hydroxide was initially dissolved in distilled water resulting in an extremely exothermic reaction.

In addition to the sodium hydroxide, in the degreasing solution are added surfactants aimed at stabilizing dissolved substances and resubmission of the grease particles on the metal surface [19].

An active ingredient in many degreasing solutions and powder detergents is sodium carbonate. This is a white, crystalline and hygroscopic powder that is used to break down grease or oil and to remove lubricants from the metal surface. Following the addition of sodium carbonate in water, an exothermic reaction occurred forming an alkaline solution consisting of carbonate anions and hydroxide groups [20].

One of the most important uses of trisodium phosphate is as a cleaning agent of surfaces which will be coated with paint, improving its adhesion to the material. Due to its high pH, it is used, in combination with a surfactant, as a component in solutions used to remove oil and grease from metal parts. Commercially, trisodium phosphate is partially hydrated and can be purchased from anhydrous trisodium phosphate to trisodium dodecahydrate phosphate. In our case, Na₂PO₄·10H₂O was added to the degreasing solution to adjust its acidity [19, 21].

Another chemical compound added to the degreasing solution, to inhibit the corrosion of carbon steel by stopping its anodic dissolution is sodium metasilicate. This is an important ingredient in industrially used detergents. Silicon content protects the metal surface from corrosion and disperses the oil/grease into solution, preventing it from being resubmission [21].

The surfactant is one of the main ingredients in the degreasing solution, and it is added to modify the properties of the liquid-solid (solution-grease) interface, thus eliminating dirt particles from the metal surface.

2.2 The pickling

Pickling is a method of treatment of the metal surface used to remove inorganic substances or rust from ferrous materials or aluminum alloys.

During steel manufacturing or processing, a layer of oxides is formed on the metal surface. These impurities can affect the use or further processing of the workpiece, such as surface plating or painting. Even though there are many methods of removing the oxide layer (sandblasting, salt baths, brushing), the most used is pickling. This extends the life of

the workpiece, smooths the surface and prepares the layer in order to deposit new layers on the metal surface [22].

The pickling rate depends on a number of variables: the base components of the pickled steel, the oxide type, the acid concentration and the ferrous chloride concentration in the solution, the temperature at which the pickling is made, the agitation, the immersion time and the presence of inhibitors [23].

In the phosphating process proposed, the pickling follows alkaline degreasing, and consist in the workpiece is introducing into a solution, made of different substances, which are presented in Table 2. The stage takes place at room temperature for a period of time of 20 minutes.

Table 2. Chemical composition of pickling solution

Substance	Hydrochloric acid [ml]	Hexamethylenetetramine [g]	Sodium sulphate [g]
Amount	300	0.9	0.3

Also known as urotropine, hexamethylenetetramine is a crystalline organic heterocyclic compound that is used in acid pickling solutions to inhibit corrosion due to its absorption on the metallic surface by electron donation. This inhibitor blocks the active sites and increases the absorption process, reducing the corrosion rate and prolonging the life of the metal with which the pickling solution comes into contact [24].

To reduce the use of aggressive acids with the environment, sodium sulphate was used as a replacement for sulfuric acid in the pickling solution [25].

Hydrochloric acid, also called muriatic acid, is an important inorganic chemical compound, widely used. Hydrochloric acid is used in carbon steel pickling operations to remove iron oxides by transforming them into soluble compounds before further processing of steel, for example: rolling, phosphating, galvanizing etc [22].

In order to protect the metal pickled by the hydrochloric acid, an inhibitor used to reduce the acid attack on the steel is added to the pickling solution, while allowing to attack the iron oxides [26].

2.3 The phosphating

The phosphating process consists in the formation of a layer of insoluble phosphate on the metal surface [27, 28]. Depending on the material which will be phosphate and the properties we want to obtain after this deposition, the substances presented in Table 3 have been added to achieve the necessary phosphating condition. In Romania, the STAS 7969-85 standard presents the main categories of phosphating solutions, the quantities and the reports which must be taken into consideration depending on their performance.

Table 3. Chemical composition of phosphate solution

Substance	Phosphoric acid [ml]	Nitric acid [ml]	Zinc [g]	Sodium hydroxide [g]	Sodium nitrite [g]	Sodium tripolyphosphate [g]
Amount	11	3	4	0.7	0.4	0.05

Taking in to account the carabiner shape and size, we considered that the most suitable method for depositing the phosphate layer is by immersing them in the phosphating solution at a temperature of 95 °Cfor 30 minutes.

The phosphate layer occurs by the formation of zinc tetrahydrate triphosphate crystals. It is made up of numerous crystals of different sizes that blend across the entire surface of

the steel as can be seen in Figure 3a. The layer also presents some designated channels and intercrystallite zones, as can be seen in Figure 3b and Figure 3c.

The surface of the carbon steel carabiner body was completely covered by the deposited zinc phosphate layer, as can be seen in Figure 3d.

Fig. 3. The deposited zinc phosphate layer microstructure a) 2kx SEM microstructure; b) 1kx SEM microstructure; c),d) EDX elemental mapping.

Due to the homogeneous covering of the carabiner surface with a non-electrical conductive phosphate layer, the component presents very low electrical discharge possibilities [29]. Therefore, by phosphate coating of personal protective equipment made of carbon steel, thus components are safe to use in potentially explosive atmospheres. Also, their corrosion properties are highly increased, despite the corrosive type of agent [13].

3 Conclusions

Carbon steel carabiners can not be used in potentially explosive atmospheres, therefore, in order to fulfill the special requirements for this application, the material surface must be covered by a homogeneous zinc phosphate layer.

Due to the zinc phosphate layer electrical insulating, in cases when the carabiner's body strikes another metal part or stones sparks formation is eliminated. Therefore, the phosphating process represents a cheap, fast and efficient method of improving the metallic personal protective equipment for potentially explosive atmosphere use.

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