Materials Research Proceedings **5** (2018) 73-77 doi: http://dx.doi.org/10.21741/9781945291814-13

Detergents for Washing of Rolling Stock

KOWALIK Pawel [1, a*], MILCZAREK Danuta [1, b]

[1] Instytut Kolejnictwa (Railway Research Institute), Materials & Structure Laboratory, Chlopickiego 50 Street, 04-275 Warsaw, Poland

[*a] kowalik@ikolej.pl, [b] dmilczarek@ikolej.pl

Keywords: Rolling Stock, Detergents, Clearing, Corrosivity, Acidic and Alkaline Agents

Abstract The article discusses acidic and alkaline cleaning agents and types of impurities removed. Their influence on paint coatings and construction elements of rolling stock is also described. It shows what contaminants occur during the operation of rolling stock exploitation and materials of carriage elements to be washed. The scope of the test and requirements for cleaning preparations for washing of rolling stock are also presented. Then, test results of the examined preparations are discussed along with the interpretation and conclusions.

Introduction

During rolling stock washing, its structural elements are exposed to aggressive substances found in the cleaning agents. Wagon boxes and chassis components are exposed to these substances. The type of preparation used depends on the impurities. The aim is to ensure that the composition of washing agents is so that their impact on the construction elements of rolling stock is as small as possible and preparation effectively removes impurities.

Rolling stock contaminants

Rolling stock contaminants can be divided into two groups:

- originating from dust deposited on the surface of rolling stock – these are mainly calcium, potassium and silicon compounds;
- arising depending on the type of traction used: iron and copper oxides, soot, oil and grease particles. Iron oxides (73%) and oils and lubricants (17%) predominate for diesel traction and iron oxides (83-90%) and mineral powders (10-16%) in the case of electric traction.

Materials of carriage elements exposed to action of cleaning agents

The external part of wagons contains elements made from steel (shell) covered with the paint coating, glass (panes), rubber (gaskets and rollers in gangways), plastics, cast iron and non-ferrous metals, mainly aluminum alloys. About 85% of the external surface of the wagons are paint coatings and about 12% are panes [1]. Paint materials are the most susceptible to dirt, among them phthalic coatings, which are relatively soft and not very resistant to acids, bases, oxidizing agents and organic solvents. The dirt is the most difficult to be removed. The most favorable in this respect are polyurethane and epoxy-ester coatings, the latter being between phthalic and polyurethane. In case of other materials, some problems are caused by some window frames made of an aluminum alloys, on which impurities accumulate easily and are difficult to remove.

Types of cleaning agents

Currently two types of cleaning agents are used: acidic (pH < 7) and alkaline (pH > 7) which remove various impurities. The use of inert (pH = 7) or slightly alkaline (pH = 7-8) agents does not give positive results. Washing preparations primarily consist of the following:

- acids or bases;
- surfactants;
- active fillers (e.g. corrosion inhibitors).

Acids and bases dissolve metal oxides and greases which make contaminations. Surfactants as surface active substances lessen water surface tension and stabilize double layer on the interface [2]. They contain two parts: hydrophilic and hydrophobic. The hydrophilic part (polar) is soluble in water and polar solvents. The hydrophobic part most often creates acidic or basic residue which dissolves action in water and polar solvents cause the formation of salt. Double action of surface active substances makes liquids containing surfactants exhibit foaming properties. Organic compounds with the polar structure of a molecule are the most often used surfactants:

- ionic – creating anions and cations as a result of dissociation in water, e. g. salts of higher carboxylic and sulphonic acids, higher amines and amine salts;
- nonionic compounds – which have in their structure polar groups that are unable to dissociate in water, e. g. higher polyhydric alcohols [3].

The selection of surfactants has a significant impact on the effectiveness of cleaning, because the lowering of water surface tension favors washing away of dirt and potential-forming compounds (acids and bases) dissolve it.

Active fillers support the action of surfactants. Their main functions are as follows: softening water (they remove calcium and magnesium ions), solution buffering, anti-corrosive action, binding of heavy metals and dispersing (breaking down into smaller particles) dirt. Most often they are chromates and organic substances absorbing on the oxide. Water cleaners have good effectiveness, are easy to use, non-flammable and relatively cheap.

Requirements for cleaning agents intended for rolling stock

The cleaning preparation should be effective and should:

- have an appropriate chemical composition (at most two acidic or basic substances with the concentration of 10-25%);
- be resistant to freezing;
- be stable after dilution;
- do not cause significant corrosion of steel and aluminum;
- do not exhibit aggressive action on paint coatings and rubber components of rail vehicle equipment.

Detailed requirements are specified in the Normative Document ND 001/07 “Cleaning agents for external and internal cleaning of rolling stock” [4].

Examination of cleaning agents for washing of rolling stock

The results of tests carried out on acidic and alkaline cleaning agents in the Railway Research Institute within the last 5 years, are presented below. The hydrochloric, sulfuric and oxalic acid were the main components of acidic cleaning preparations. Sodium hydroxide and potassium hydroxide were the predominant components in case of alkaline agents. The scope of research included among others the following tests:

- determination of pH value according to ISO 1262:2004 [5];
- determination of corrosive action on steel and aluminum according to ND 001/07 [4];
- determination of the impact on hardness change of material intended for doors and windows gaskets (rubber) according to PS-C-04238:1980 [6];
- determination of tensile strength of materials intended for doors and windows gaskets (rubber) according to ISO 37:2007 [7];
- determination of aggressive action on paint coatings according to ISO 2812-3:2012 [8].

Tests results

The results of test conducted on acidic and alkaline cleaning agents are depicted below accordingly in Table 1 and Table 2.

Table 1. Results of the tests of acidic cleaning agents (detailed results are in the possession of Materials & Structure Laboratory – Railway Research Institute)

Type of examination	Agent 1*	Agent 2*	Agent 3*	Agent 4**	Agent 5*	Agent 6***	Value required by ND 001/07
pH value [pH]	2.6	1.0	1.6	1.4	1.0	1.0	≥ 1
aggressive action on steel [g/m^2]	35.4	29.9	14.4	40.1	14.7	14.1	≤ 120
aggressive action on aluminum [g/m^2]	19.7	19.8	1.8	15.5	5.7	6.9	≤ 20
aggressive action on rubber elements – impact on change of rubber hardness [%]	1.6	0.0	0.0	1.6	4.5	4,5	≤ 15%
aggressive action on rubber elements – impact on change of tensile strength of rubber [%]	0.0	4.,1	1.7	1.1	8.0	8.3	≤ 15%
aggressive action on paint coatings I–IV	I: no change II: no change III: light dulling IV: no change	I: no change II: no change III: light dulling IV: no change	I: no change II: no change III: no change IV: no change	I: no change II: no change III: light dulling IV: no change	I: no change II: no change III: light dulling IV: no change	I: no change II: no change III: light dulling IV: no change	permissible light dulling or slight discoloration

*agents on a basis of hydrochloric acid, **agent on a basis of sulfuric acid, ***agent on a basis of oxalic acid
I – polyurethane coating (green), II – epoxy-acrylic coating (blue), III – phthalate coating (blue), IV – epoxy-polyurethane coating (blue).

Discussing the results and conclusions

The examined preparations have acidic and alkaline pH. Knowledge of pH value of cleaning preparations is important when predicting processes such as metals and paint coatings corrosion.

Aggressive (corrosive) effect on steel and aluminum

Iron and aluminum alloys are the most important construction materials of a rail vehicle exposed to corrosive action of washing agents. Corrosion cause transformation of metals and their alloys in nonmetallic compounds (oxides and hydroxides) and if not inhibited corrosion may lead to weakening of the quality of carriage boxes construction.

Corrosive processes of steel depend on the concentration of hydrogen ions [H+] in the electrolyte acting on it. The course of this phenomenon is presented by the equations of reactions [9]:

$Fe \rightarrow Fe^{2+} + 2e^-$ (iron ionization under water impact) (1)

$2e^- + 2H^+ \rightarrow 2H$ (hydrogen ions capture electrons) (2)

$2H + 1/2\ O_2 \rightarrow H_2O$ (reaction of hydrogen atoms with oxygen from the air) (3)

$Fe + H_2O + 1/2O_2 \rightarrow Fe^{2+} + 2OH^-$ (summary course of the reaction) (4)

In an alkaline environment the above reaction proceeds to a minimal extent, because in accordance with Le Chatelier rule OH^- ions shift the equilibrium state of the reaction (4) to the left. That is why in the presence of a base the corrosion process is ceased.

Table 2. Results of the tests of new alkaline cleaning agents (detailed results are in the possession of Materials & Structure Laboratory – Railway Research Institute)

Type of examination	Agent 7**	Agent 8*	Agent 9*	Agent 10**	Value required by ND 001/07
pH value [pH]	13.0	13.0	11.0	12.3	≤ 13
aggressive action on steel [g/m^2]	1.2	0.9	5.1	0.9	≤ 120
aggressive action on aluminum [g/m^2]	10.8	12.1	6.4	12.5	≤ 20
aggressive action on rubber elements – impact on change of rubber hardness [%]	2.9	1.6	1.6	3.1	≤ 15%
aggressive action on rubber elements – impact on change of tensile strength of rubber [%]	18.3	10.8	13.2	2.9	≤ 15%
aggressive action on paint coatings I–IV	I: no change II: light dulling III: dulling IV: no change	I: no change II: no change III: dulling IV: no change	I: no change II: no change III: dulling IV: no change	I: no change II: light dulling III: dulling IV: no change	permissible light dulling or slight discoloration

*agents on a basis of sodium hydroxide, **agents on a basis of potassium hydroxide
I – polyurethane coating (green), II – epoxy-acrylic coating (blue), III – phthalate coating (blue), IV – epoxy-polyurethane coating (blue).

In an acidic environment the state of equilibrium of the reaction (1) shifts to the right towards the formation of Fe^{2+} ions as a result of electrons consumption in reduction of hydrogen in acidic electrolyte. Favoring the formation of Fe^{2+} ions develops the corrosion process. Therefore, acidic cleaning agents are more aggressive to steel than alkaline preparations.

The above analysis is in agreement with the obtained test results. The examined alkaline preparations showed significantly lower aggressiveness to steel than acidic preparations.

Aluminum, on the other hand, is an amphoteric element that reacts with both acids and bases. In a natural environment it spontaneously covers the surface with an oxide layer that protects against corrosion:

$$2Al + O_2 \rightarrow Al_2O_3 \quad (5)$$

Only the damage of the resulting protective layer, under the influence of some acids and strong bases solutions, may induce further course of corrosion process. This is the reason why it is difficult to predict in which environment the corrosion process will be more intense.

This was confirmed in the test results. Similar values of mass losses of aluminum samples were obtained in case of acidic preparations (agents 1, 2 and 4) as well as for alkaline preparations (agents 7, 8 and 10).

Aggressive action on paint coatings. The tested agents, both acidic and alkaline, showed no aggressive action on the surface of the tested coating samples. No changes were observed after a 24 h action of cleaning products. The exception was phthalic coating (blue), where there was a light dulling on the surface of the tested coating under the influence of acidic preparations and dulling under the influence of alkaline preparations. The study showed that phthalic coatings are indeed less resistant to action of strong acids and strong bases solutions than the other paint coatings.

Aggressive action on rubber elements. The obtained results of the experiments show that both alkaline and acidic preparations do not significantly change the hardness of rubber, constituting structural elements of carriages.

It is different in when it comes to changes of the tensile strength of rubber. Acidic agents showed little effect here, within the limit permitted by ND 001/07 [4]. Alkaline agents showed various impact (preparations 7 and 10). The main component of both preparations was potassium hydroxide of similar concentrations (2-5%). Despite this fact, agent 7 changed the tensile strength of rubber by 18,3% and agent 10 only by 2,9%. Agent 7 does not meet the requirements of ND 001/07 [4]. Such a big difference is probably caused by the influence of other ingredients in both preparations.

Summary

The examination of currently used and new acidic and alkaline cleaning preparations for rolling stock showed slight aggressive action (apart from agent 7) for structural elements of rolling stock and meet the requirements of ND 001/07 [4]. It is assessed that introduction for use of preparations systematically modified by manufacturers influenced the following: lengthening the life of used railway vehicles, reducing pressure on environment and reducing the exploitation costs.

References

[1] M. Moczarski Washing of passengers carriages in a depot and the environmental hazard, Railway Reports, 144 (2007) (in Polish).

[2] L. Pajdowski General chemistry, Polish Scientific Publishing House (1985) (in Polish).

[3] T. Kalak Influence of surface properties of washing powder solutions on their washing abilities, doctoral dissertation, University of Economy (2012) (in Polish).

[4] Normative Document ND 001/07 Cleaning agents intended for external and internal washing of rolling stock, Railway Scientific and Technical Center/Railway Institute (2007) (in Polish).

[5] ISO 1262:2004 Surface active agents. Determination of pH value of solutions and dispersions.

[6] PS-C-04238:1980 Rubber. Determination of hardness according to Shore method.

[7] ISO 37:2007 Rubber, vulcanized or thermoplastic. Determination of tensile stress – strain properties.

[8] ISO 2812-3:2012 Paints and varnishes. Determination of resistance to liquids. Part 3: Method using an absorbent medium.

[9] K. M. Pazdro Chemistry. Educational Outbuilding (1995) (in Polish).