



The impact of lubricants used in the rubber industry on the quality of generated wastewater. Recycling of lubricants in the production process

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ABSTRACT

The study presents research on the impact of lubricants on the quality of wastewater generated in a plant producing rubber hoses and the possibility of recovering and returning these agents to the production process. The research was carried out at the Hutchinson Żywiec 2 plant (Southern Poland). There were six different lubricants with different performance properties tested. The lubricants from the Rheolease series with the numbers 4834, 2544G, 3241 DV, and 487LG produced by performance fluid (Performance Fluids Ltd., Unit 1, Hodge Bank Business Park, Reedyford Road, Nelson BB9 8TF, United Kingdom) and the lubricants from the Struktol series with the numbers XP6253 and XP6245 produced by Schill+Seilacher (Schill+Seilacher GmbH, Schoenaicher Str. 205, 71032 Boeblingen, Germany) were tested when dissolved in deionized water. It was observed that the lowest concentrations of chemical oxygen demand (COD) and non-ionic surface-active agents (SAAs) were achieved in the aqueous solution containing Struktol XP6245. However, due to unfavorable process parameters (unpleasant odor), the Rheolease series lubricants were used in the technological process. Tests conducted on actual wastewater containing these lubricants showed that for Rheolease 487LG lubricant, the lowest COD and non-ionic SAAs concentrations were achieved, measuring 283 and 144 mg/L, respectively. Furthermore, for the same recycled lubricant, lower COD concentrations were obtained compared to the new lubricant, measuring 28,600 and 46,530 mg/L, respectively.

Keywords: Rubber release agents; Rubber lubricants; Non-ionic surfactants; Chemical oxygen demand; Lubricants recycling

1. Introduction

Irrespective of the sector, the extraction of rubber from molds or the detachment of rubber from mandrels constitutes a pivotal phase in the rubber product molding process during vulcanization. Modern anti-adhesive agents facilitate the swift, effortless, and clean disengagement of rubber components from molds or steel mandrels, sparing operators excessive exertion while safeguarding the integrity of the products. In instances where parts fail to separate adequately from molds, manufacturers can anticipate

shortages, unanticipated downtimes, escalated material expenditures, augmented labor, transportation, and energy outlays, in addition to heightened strain on equipment and increased intricacies in the processes. As a result, lubricants assume a paramount role in the rubber industry.

Lubricants are employed in the vulcanization process for the following purposes:

- As a coating lubricant for steel mandrels, enhancing slip and facilitating the application of rubber hoses by mitigating frictional resistance. Moreover,

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they provide protection against mechanical harm to the rubber during the manual application of hoses to mandrels.

- As releasing agents for rubber after the vulcanization procedure. They shield the rubber from adhering to the surface of steel mandrels, averting instances of rubber adhering to the mandrels, thereby simplifying removal after vulcanization process.

Improving the quality of rubber release agents allows manufacturers to produce more parts with reduced cycle times and lower scrap rates [1,2].

Regrettably, owing to their function, these agents are characterized by substantial surfactant content, resulting in industrial wastewater from rubber processing establishments carrying elevated concentrations of toxic substances that prove deleterious to aquatic ecosystems. The presence of surfactants in effluents channeled into biological wastewater treatment plants can disrupt their operation, possibly leading to the demise of activated sludge and halting the wastewater treatment process. While surfactants are generally nontoxic to mammals, they exert significant toxicity on aquatic organisms, including microorganisms in the activated sludge of biological wastewater treatment facilities. Concentrations of surfactants exceeding 0.313 mg/L have been shown to cause foam-induced damage to activated sludge [3,4].

Surface-active agents are divided into ionic surfactants (anionic, cationic, ampholytic) and non-ionic surfactants. In order for a manufacturing plant to discharge post-process wastewater into the sewage system, it must ensure that the wastewater has the right parameters. In the case in question, the lubricants caused a high content of non-ionic surfactants. Therefore, in order to reduce the concentration of chemical oxygen demand (COD) and non-ionic surface-active agents (SAAs) in the discharged wastewater, it is necessary to select for the production process a lubricant that will cause the lowest possible content in the wastewater. Nonetheless, the wastewater has to be properly treated before being discharged into the sewage system.

Known methods used to treat such wastewater are coagulation [5], chemical oxidation [6], sorption [7],

flotation [8], biodegradation, membrane processes [9] or evaporation [10]. Depending on the substances that are in the wastewater, these methods can vary in effectiveness.

The challenge for the rubber industry is the selection of anti-adhesive agents used during the production cycle in a manner that minimizes their presence in the generated wastewater. In contemporary times, the 2030 Agenda for Sustainable Development presents manufacturing enterprises with substantial challenges in aligning with its objectives. Consequently, it is imperative to curtail pollution, rationalize water resource consumption, and implement circular economy principles across all dimensions [11].

The objective of this research endeavor was to appraise diverse lubricants, juxtapose their performance attributes, and evaluate their influence on the characteristics of the generated wastewater.

2. Materials and methods

The research consisted of three stages:

- Testing fresh, unused lubricants;
- Analyze of wastewater obtained from washing vulcanized rubber hoses after using various lubricants;
- Testing of the selected recycled lubricant.

2.1. Fresh mandrels lubricants

Six different lubricants from two manufacturers were selected for the study:

- Performance Fluid (Performance Fluids Ltd., Unit 1, Hodge Bank Business Park, Reedyford Road, Nelson BB9 8TF, United Kingdom)
- Schill+Seilacher (Schill+Seilacher GmbH, Schoenaicher Str. 205, 71032 Boeblingen, Germany)

These lubricants are generally available on the market and dedicated specifically to the rubber industry. These release agents are polymer blends and polyol block copolymers. The list of the tested measures and their features is presented in Table 1 [12].

Table 1
List of lubricants used in the test

No.	Producer	Type of lubricant	Characteristics
1	Performance fluid	Rheolease 4834	Appearance: light yellow fluid, solubility in water: complete, relative density 1.06; Acute toxicity: <i>Daphnia magna</i> Test OECD 202 EC 50 24h > 1,500 mg/L
2	Performance fluid	Rheolease 2544G	Appearance: white gel, solubility in water: complete, relative density 1.15; Acute toxicity: <i>Daphnia magna</i> Test OECD 202 EC 50 24h > 1,500 mg/L
3	Performance fluid	Rheolease 3241 DV	Appearance: yellow viscous liquid, solubility in water: complete: relative density 1.27; Acute toxicity: <i>Daphnia magna</i> Test OECD 202 EC 50 24 h > 1,500 mg/L
4	Performance fluid	Rheolease 487LG	Appearance: light yellow wax solubility in water: complete, relative density 1.05; Acute toxicity: <i>Daphnia magna</i> Test OECD 202 EC 50 24 h > 1,500 mg/L
5	Schill+Seilacher (Germany)	Struktol XP6253	Appearance: light yellow wax, solubility in water: complete, relative density 1.05; Acute toxicity: <i>Daphnia magna</i> Test OECD 202 EC 50 24 h > 1,500 mg/L
6	Schill+Seilacher (Germany)	Struktol XP6245	Appearance: light yellow fluid solubility in water: complete, relative density 1.10; Acute toxicity: <i>Daphnia magna</i> Test OECD 202 EC 50 24 h > 1,500 mg/L

The research consisted in analyzing the concentrations of COD and non-ionic surfactants (non-ionic SAAs) in new, unused lubricants. COD is an arbitrary indicator of the content of organic and inorganic compounds in the analyzed solution and can be a determinant of sewage toxicity. In order to perform the tests, identical samples of solutions containing 100g of each lubricant dissolved in 5 L of distilled water were prepared. An equal amount of each lubricant was measured using a digital scale BLOW JS13 0.1 – 3000g. Samples analysis was performed in the accredited SGS Polska laboratory in Pszczyna using the following methods: spectrophotometric PN-ISO 15705:2005 (A) and the method of continuous flow analysis (CFA) with spectrophotometric detection PN-EN ISO 16265:2012 (A), (NR).

2.2. Wastewater from the process of washing vulcanized rubber hoses

The research took place in production hall No. 3 at the Hutchinson Żywiec 2 plant. This area houses 8 steam autoclaves used for the vulcanization of rubber hoses, as well as 6 machines dedicated to washing the rubber hoses following the vulcanization process. To assess the concentrations of specific substances, wastewater samples were gathered from a collection sump. This sump serves as a central point where wastewater from all washing machines within Production Hall No. 3 converges after the washing procedures.

At this designated collection point, wastewater was gathered from all washing stations within Production Hall No. 3. This collection was facilitated by an automatic sampling device known as an autosampler, Teledyne ISCO Avalanche 6712. This device is designed to automatically collect 0.5 L of sewage every hour, allowing for the accumulation of up to 24 samples. In total, 24 samples were obtained for analysis, representing an average daily sampling.

The collected samples were sent to the accredited SGS laboratory in Pszczyna, where the COD and non-ionic SAAs values were determined. These parameters were tested using the following methods: spectrophotometric PN-ISO 15705:2005 (A) and the method of continuous flow analysis (CFA) with spectrophotometric detection PN-EN ISO 16265:2012 (A), (NR).

2.3. Recycled lubricant

The recycled lubricant tested is Rheolease 487LG. This rubber release agent proved to be the most favorable in the previous trials, which is why this agent was selected for the next test.

In the course of regular plant operations, surplus lubricant is known to trickle from rubber mandrels, accumulating within the dripping tubs located beneath the bottom trolley. Within these receptacles, a composite mixture forms, comprising both pristine agent predating the vulcanization process, as well as spent agent after vulcanization. This superfluous blend is subsequently amassed within steel barrels and managed as waste material. As a component of the conducted study, a singular 200 kg barrel underwent mechanical filtration and was subsequently used again for the production process. This measure was taken to evaluate the applicability of the lubricant procured through this method.

Within the scope of the study, solutions were meticulously prepared by dissolving 100 g of fresh lubricant in 5 L of distilled water, alongside an analogous formulation featuring 100 g of recycled lubricant within the same 5 L of distilled water. Subsequently, the samples, thus prepared, were dispatched to the accredited SGS Laboratory located in Pszczyna. The objective of this submission was to facilitate the quantification of concentrations pertaining to noteworthy COD and non-ionic SAAs parameters. The assessment of these parameters was executed employing the subsequent methodologies: the spectrophotometric approach as delineated in PN-ISO 15705:2005 (A), supplemented by the continuous flow analysis (CFA) technique featuring spectrophotometric detection as specified in PN-EN ISO 16265:2012 (A), (NR).

3. Results and discussion

3.1. Agents for lubricating mandrels

Table 2 presents the results of tests for the content of COD and non-ionic SAAs in samples of solutions of individual lubricants in distilled water.

The summary presented in the table above shows that the lowest concentrations of COD and non-ionic SAAs are contained in the Struktol XP6245 sample, and the highest concentrations of these parameters characterize the Rheolease 4834 liquid lubricant used so far in the production process. This confirms the observation that during the preparation of samples for testing, the mixture containing Rheolease 4834 showed the greatest foaming, and the resulting foam persisted for a longer time.

The obtained results also show a correlation between the tested parameters. With increased values of COD, also the concentration of non-ionic SAAs in the sample is higher. It can therefore be concluded that the COD in the samples of the tested lubricant solutions results directly from the amount of surfactants contained in them.

The lubricant showing the lowest COD and non-ionic SAAs values, Struktol XP6245 stood out from the other agents with a very specific, unpleasant smell, which made working with it very difficult.

3.2. Wastewater from the washing process of rubber hoses

Table 3 presents the results of testing the content of COD and non-ionic SAAs in wastewater samples from the

Table 2
Summary of test results for samples of solutions of various lubricants

No.	Sample of lubricant	Chemical oxygen demand (mg/L)	Surface-active agents (mg/L)
1	Rheolease 487LG	47,020	18,000
2	Rheolease 4834	50,000	22,900
3	Rheolease 3241 DV	32,160	11,200
4	Rheolease 2544G	38,710	21,250
5	Struktol XP6253	37,770	11,664
6	Struktol XP6245	28,915	7,887

process of washing rubber hoses after the vulcanization process.

During the first days of testing, the lubricants from position 5 and 6 of Table 3 were disqualified for technological reasons. In the first test, these lubricants turned out to be the most favorable due to environmental conditions, they showed the lowest COD and non-ionic SAAs concentrations. Unfortunately their technological properties did not work in the production process. During operation with the use of these lubricants, the rubber after the vulcanization process strongly adhered to the steel mandrels, making it difficult to remove it. In many cases, the pieces could not be removed at all without damage, and the mandrels had to be cleaned after each vulcanization cycle. Therefore, the continuation of these studies was abandoned and no effluent test results were obtained when using these two lubricants.

The acquired findings further demonstrate a notable disparity in concentrations across distinct parameters, contingent on the type of lubricants used. Notably, COD concentrations within the collected wastewater span from 283 to 1,038 mg/L, while non-ionic SAAs concentrations

exhibit a range of 144 to 704 mg/L. Throughout the experimentation, measures were implemented to ensure the consistency of outcomes across various lubricants. This was achieved through the uniform loading of all rubber hose washing machines subsequent to the vulcanization process. To clarify, each washing cycle involved the introduction of 5 complete bags containing rubber hoses into each respective washing machine.

Despite meticulous arrangements, the preservation of identical testing conditions during regular production proved unattainable. As a result, the presented results embody a certain degree of averaged values. Nevertheless, considering the inherent variations within normal production processes, these outcomes can be deemed reliable representations of the routine functioning of the production facility.

3.3. Recycled lubricant

Table 4 shows the results of a sample analysis comparing fresh Rheolease 487LG lubricant and the same recycled lubricant.

Testing the parameters of the recycled lubricant showed its full functionality in the production process. During the use of the recycled lubricant, no characteristics were observed that would negatively affect its suitability in the process. This lubricant spread well and ensured good slippage when applying rubber hoses to steel mandrels, as well as enabling easy removal of pieces from modeling fittings after the vulcanization process.

The comparative analysis between the parameters of the recycled lubricant and its pristine counterpart underscored the environmental benefits of its reuse. Recycled lubricant showcased significantly diminished concentrations of both COD and 5-day biochemical oxygen demand, signifying its positive impact from an ecological perspective.

The confirmation of the recycled lubricant's functionality, coupled with its advantageous influence on process-derived wastewater, constitutes a valuable outcome of the conducted investigation. The potential for lubricant reuse,

Table 3

Summary of the results of wastewater tests from the process of washing rubber hoses after using various lubricants in the vulcanization process

No.	Sample of wastewater from washing of rubber hoses	Chemical oxygen demand (mg/L)	Non-ionic surfactants (mg/L)
1	Rheolease 4834	1038	704
2	Rheolease 2544G	884	293
3	Rheolease 3241 DV	589	174
4	Rheolease 487LG	283	144
5	Struktol XP6253	NA	NA
6	Struktol XP6245	NA	NA

NA – not analyzed

Table 4

List of test results for the parameters of the new and recycled Rheolease 487LG lubricant

Parameter	New lubricant	Lubricant after filtration
Petroleum hydrocarbons, mg/L	4.3	27
Substances extractable with petroleum ether, mg/L	1,040	2,700
Nitrite–nitrogen, mg/L	0.15	<0.1
Ammonium nitrogen, mg/L	<0.5	<0.5
General chrome, mg/L	<0.0020	0.0093
Lead, mg/L	<0.005	<0.005
Copper, mg/L	0.066	0.047
Zinc, mg/L	0.06	0.63
5-day biochemical oxygen demand, mg/L	17,800	14,400
Chemical oxygen demand, mg/L	46,530	28,600
Total nitrogen, mg/L	286	372
Total suspended solids, mg/L	2,200	2,600
Total phosphorus, mg/L	178	54

Table 5
Annual amount of wastewater from the process of washing rubber hoses after the vulcanization process and the amount of lubricant used

Year	Quantity of wastewater from washing process	Quantity of lubricant used
2022	47,000 m ³	147 Mg

mitigating the need for new acquisitions, carries substantial economic and environmental implications. The yearly volumes of lubricant usage and corresponding wastewater volumes are outlined in Table 5.

4. Conclusions

The findings from the study illustrate that the application of Rheolease 4834 agent within the production process results in the highest concentrations of COD and non-ionic SAAs within the technological wastewater. Conversely, the lowest concentrations of COD and non-ionic SAAs in the said wastewater were observed when the Rheolease 487LG agent was used. Comparing the parameter values across the rubber release agents themselves, a noteworthy disparity emerged when examining the corresponding parameters within the acquired wastewater from the production processes. It's important to note that the outcomes are influenced not only by the properties of the lubricant but also by the method employed for its application onto the rubber modeling mandrels, which differs between solid and liquid lubricants. In the case of liquid lubricants, application involves the use of spray guns, while solid lubricants are administered through brushes. This dichotomy can lead to variations where the employment of spray guns might yield higher lubricant quantities on the mandrels and their fittings, subsequently influencing the concentrations of the analyzed parameters within the generated wastewater.

The second significant reason affecting the results is the human factor. In the tests carried out, lubricants were dosed manually, so the amounts of lubricants used, which were applied to the rubber molding mandrels, were not necessarily the same and repeatable. It should be noted, however, that in the production plant in question, experienced people with long experience work as autoclave operators and during the research there were no changes in staff, which to some extent ensures the credibility of the results obtained.

The last factor that may affect the results may be the reactions occurring in the lubricants themselves after contact with the steel mandrels and rubber as a subjected to high temperature (180°C) during the vulcanization process.

As a result of the tests carried out and after analyzing the results in the production plant, it was decided to change the technology and the hitherto used agent Rheolease 4834 was replaced with the agent from the same manufacturer, Rheolease 487LG, and as another improvement, recycling of this lubricant was introduced. Thanks to these technological changes, the concentration of non-ionic SAAs in the wastewater from the process of washing the vulcanized

rubber hoses was reduced several times from the original values (600–700 mg/L) to the value (130–200 mg/L).

Despite the obtained significant reduction of the analyzed parameters of COD and non-ionic SAAs, the wastewater obtained is still toxic and cannot be discharged directly to sewage systems. In order to be able to transfer this wastewater to the municipal biological treatment plant, it is necessary to pre-treat it and reduce the analyzed parameters to levels safe for the treatment plant, that is, to the non-ionic SAAs value <20 mg/L. The methods that can be used for this purpose are wastewater pretreatment by adsorption with activated carbon or membrane ultrafiltration [13,14].

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