

A Practical Approach to Cleaning Molds from Rubber Residues

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Abstract: - In this paper, methods of fouling prevention and cleaning of the molds from vulcanized rubber residues are presented. The surface free energy of mold surfaces has been measured and the mold release agents were compared by measuring the force needed for the release of the form. The efficiency of sodium hydroxide solvent currently used for mold cleaning in industrial practice is compared with an acid-based solvent. The effect of the acid on the mold surface is monitored as well. The relative mass loss and the change in the surface roughness parameters Sa and Sz were evaluated during the corrosion testing in the acid at various temperatures. The mold wear during a year of use in the company, and a year of continuous acid exposure was then extrapolated for steel and stainless-steel molds. Nitric acid was significantly more effective than NaOH in dissolving rubber with full dissolution occurring after 3 h at 80 °C when stirred, losing 33 % of its initial mass, while NaOH lost only 0.3 % after 24 h. Stainless steel proved very resistant to acid corrosion at 50 °C with a calculated loss of 0.003 cm of thickness per year of submersion, while 1.7131 steel would lose 0.264 cm of thickness.

Key-Words: - steel molds, cleaning, solvents, vulcanized rubber, corrosion, surface roughness

1 Introduction

Mold cleaning is an important part of rubber processing. Both molds and their parts such as clogged vents should be cleaned regularly. Due to synthetic materials used in modern tire compounds, cleaning is further complicated by mold fouling formed within each production cycle from both organic and inorganic materials leaving a small deposit of residues. For tire molds, this can represent 1000 to 3000 layers of organic and inorganic compounds that need to be removed [1]. Monitoring the proper time for the cleaning is essential, and thus it was a subject of research by Kim et al. [2], who studied how to measure temperature and pressure changes in the mold cavity to do so effectively.

The easiest cleaning method is mechanical pulling off with/without a cleaning knife. This method is, however, useable only for simple molds and screws and easily removable residues. Then, if all precautions against pollution and accidents are observed, all thermoplastic and thermosets may be also removed thermally. Examples include flaming or the treatment of a mold in an oven. However, the oxidation and carbonization of the mold surface is an inherent risk for this method [3].

Ultrasonic solvent cleaning is a method recommended by Fragassa et al. [1] as the best solution for cleaning tire molds while preserving their functionality. Other methods, such as laser

cleaning and cleaning with dry ice have been investigated as well and are nowadays utilized in practice [3].

Open solvent baths are also often used, while closed solvent baths are utilized when no other options are available due to their high costs. Furthermore, in most cases, oil bath cleaning yields similar results, and solvents need to be selected for a given material [3].

The complexity of these methods stems mainly from the crosslinked structure of the rubber and similar elastomers, which prevents simple recycling as can be done for thermoplastics [4], [5]. After vulcanization, the biodegradability of latex, for example, is lost [6]. To decrease this chemical resistance, devulcanization processes were studied. Devulcanization often aims to selectively cleave C-S bonds, while leaving C-C bonds intact. For this purpose, the precise amount of energy to break up the rubber structure needs to be applied. Sun et al. [7], studied continuous ultrasonic devulcanization [6] finding that the ultrasonic amplitude plays role in the devulcanization efficiency.

Dogadkin et al. [8], [9] found out that vulcanized rubber is soluble in xylene if molecular oxygen is passed through at elevated temperatures. Butadiene-styrene rubber (SBR) is less soluble than natural rubber (NR). This process can be however dangerous. Chemical methods based on the oxidation of sulfur bonds using nitric acid (HNO₃) and benzoyl-

peroxide ($C_{14}H_{10}O_4$) were also studied and were selected as the methods most likely to solve the specific scope of our work [10]–[12]. These methods were however tested mainly on pure rubbers without fillers. In practice, fillers such as carbon black (CB) are very common. The efficiency of this approach on the specific industrial product was therefore evaluated.

This paper presents the results of a study aimed at cleaning molds in the practice. Laser, dry ice, and ultrasonic cleaning were found lacking in some way, mainly due to factors such as price and noise. Solvent cleaning was chosen as the best option for this research. To our best knowledge, especially in the field of solvent cleaning, there was little done on the effects of nitric acid on vulcanized rubber, and to our best knowledge, no article combined it with an investigation on the effect of this solvent on fouled material itself.

2 Problem Formulation

The aim of the research was to find a way to either prevent fouling and/or make form cleaning more efficient for the specific industrial application. The current process includes mechanical cleaning followed by 24 h boiling in NaOH (18 % aq.) bath, sandblasting with plastics, ultrasonic bath, and naphtha treatment of mold surface. This is both a complicated and time-consuming process, and even more, it results in the loss of the first 3 to 4 batches due to the recrystallization of NaOH on the mold surface during the further manufacturing cycle.

2.1 Materials and Methods

Utilized rubber was an NR/SBR compound with carbon black (CB) filler. The effect of NaOH solutions, both prepared in the laboratory (18 % aq.) and taken directly from the solvent bath in the particular production, was compared with concentrated (65 %) HNO_3 . A 4:1 ratio of acid to rubber was needed as the 2:1 ratio proved insufficient to dissolve all of the rubber. Pieces of 2 mm thick and 2 cm long rubber were used. Devulcanization trials used a standard reflux setup with a 50 ml flask, heated oil bath, stirrer, condenser, and thermometer. The soluble fraction was then strained out and the solids dried first 24 h at 50 °C, and then vacuum dried at 80 °C for 4 h and weighed.

The effect of the chosen chemicals on the mold steel of 1.7131 grade (1.7131) and BÖHLER M303 High Hard (M303HH) stainless steel, corrosion was also investigated. Surface roughness at the start, in

the middle, and at the end of the testing was measured.

For this purpose, Ametek NewView™ 8000 3D optical surface profiler was employed.

The tests of rubber to mold adhesion were done on ZWICK Materialprüfung 1456 (ZwickRoell GmbH & Co.KG) with two mold release agents Lusin Alro OL 151 and MONO-COAT® 418W, and with only the isopropyl alcohol cleaned surface. Surface free energy was tested with a Drop Shape Analyzer Krüss DSA30 with included Top-view TVA module (Krüss GmbH).

3 Problem Solution

Due to the complex shape of the mold, only the Top View Sessile Drop method and ethylene glycol as a drop phase and air as the surrounding medium was used. Other common drop phases could not be used due to the method limitations. The surface free energy of 1.7131 steel was 44.22 mN/m and chromium part 44.01 mN/m. As SBR rubber has, according to the literature [13], free energy closer to measured values than NR, using greater wt. % of NR in the compound was suggested. Better results were confirmed in practice; however, this solution is infeasible due to the increase in the cost of material used.

Adhesion tests showed that MR MONO-COAT® 418W provided the lowest adhesion strength of 73 N. Cleaned surface was second-best at 93 N and multipurpose MR Lusin increased this strength to 233 N. This research direction was therefore abandoned.

Solvent testing has shown nearly complete ineffectiveness of NaOH as a solvent as the investigated rubber lost only 0.3 % of its total mass by the end of the experiment. There was also no significant difference on the surface of the rubber samples before and after 24 h of boiling in this solvent. On the contrary, it took 3 h at 80 °C for the nitric acid, when stirred, to dissolve rubber to dust containing mainly CB and the remaining polymeric fraction. This residue had only 67 % of the initial mass. To achieve comparable effects, it took 4h without stirring (64 % of the initial mass). The temperature at 50 °C with stirring for 12 h resulted in 73 % of the initial mass remaining (6 h resulted in 74 %). If the sample was over-vulcanized for 100 h at 175 °C and dissolved at 80 °C (simulating a piece of rubber stuck in the machine for the entire working week) it resulted in 64 % of the initial mass. Small pieces of residue were left even after 12 h of dissolving these over-vulcanized samples if 50 °C temperature was used and 86 % of the initial mass

was left. Room temperature (RT) acid will not fully dissolve such large pieces of even standardly vulcanized rubber in 24 h, however, its effect is greater than NaOH as it lost 10.8 % of its mass. For comparison, if benzoyl peroxide was used instead of nitric acid, natural rubber had a degree of devulcanization of 46.8 % after 6 h at 80 °C as presented by Rooj et al. [12]. This, however, only proves that both solvents are effective, as Rooj focused on the degree of devulcanization, while our work on the mass loss. Alternatively, we can assert that our CB-filled NR/SBR rubber was harder to dissolve than the SBR compound used by Rios et al. [11] who also used 80 °C HNO₃ and a reflux system with a 1:2 rubber:acid ratio. They achieved 35 % mass loss after only 2 h.

From these findings, 80 °C is the sufficient temperature for dissolution of both standard vulcanized rubber and over-vulcanized samples, while 50 °C is not sufficient to fully dissolve some over-vulcanized residues which may occur in the production. The reason for this is likely oversaturation of the carbon at the surface of the rubber piece throughout the experiment, which partially passivates it. Colder acid is then unable to attack rubber molecules effectively. The 3 h dwell at 80 °C is therefore recommended from this standpoint.

For this specific type of rubber, we can therefore assert that approximately 70 % of the initial mass is a point where the rubber will be fully dissolved to point of disintegration. We consider 50 °C as a temperature, where the rubber can be dissolved to 74 % of the initial mass after 6 h, while after 24 h still to 73 % and any leftover, needle-thin, aggregates which however broke apart at a touch. An interesting case was over-vulcanized samples, which broke into smaller pieces though they had still a lot of initial mass left. These samples fractured and partially dissolved at the same time.

All these results show the importance of the temperature and vulcanization degree and to a lesser degree the importance of stirring. Preferred temperatures for full cleaning and devulcanization of this type of rubber are therefore ≥ 50 °C. The effect of room temperature acid on molds is, therefore, less important but still included as it provides better results than NaOH.

The results of the corrosion tests show significant loss of the bulk of 1.7131 steel, around 0.7 % for 50 °C HNO₃. Mass loss was recalculated to the loss in thickness according to Eq. 1 and 2:

$$V = \frac{m}{\rho} \quad (1)$$

$$l_0 - l_e = \left(\sqrt[3]{V_0}\right) - \left(\sqrt[3]{V_e}\right) \quad (2)$$

where: ρ – density of steel; m – the mass of sample; l_0 and l_e initial and final thickness of the cubic sample. The initial density of 1.7131 and M303HH steels were 7.85 and 7.72 g/cm³, respectively, as per their material datasheets.

This 0.7 % then equals the loss of approx. 0.005 cm thickness of the sample during the 156 h long experiment. Per year (365 days) at 50 °C, 1.7131 steel mold would then lose 0.264 cm of thickness. However, this represents over 50 years' worth of stress as molds in this company are cleaned weekly, while the results of 156 h experiment represent 1 year of cleaning with 3 h acid bath time - therefore the approximate stress mold should undergo during the regular yearly use (RYU) at those conditions. Results for RYU and the overall progress of corrosion can be seen in Fig. 1. Each cycle there represents 6 h of dwell time in acid – twice the recommended time in acid.

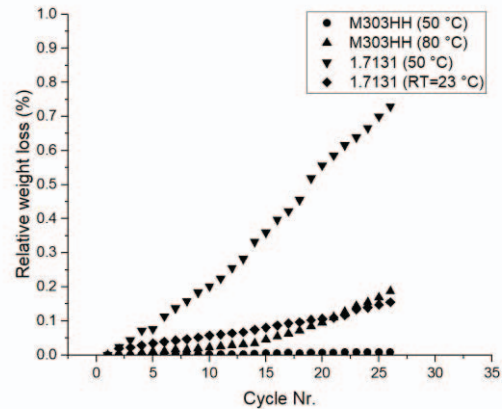


Fig. 1 Results of corrosion testing in Nitric Acid for 1.7131-grade steel and M303HH stainless steel.

In contrast to 1.7131 steel, results show that M303HH stainless steel would lose only 0.003 cm of thickness submerged in 50 °C nitric acid for a full year, time outside not counted, when cyclically stressed this way. Stainless steel in the acid at 80 °C loses 0.067 cm of thickness and 1.7131 steel at RT 0.057 cm per full year, and both can be considered somewhat resistant at these temperatures.

As can be seen in Table 1, surface roughness for 50 °C M303HH steel, the same as 1.7131 steel at RT, was lower at the end of the corrosion testing, and both at 50 °C and 80 °C a visible layer of magnetite was observed to develop on M303HH steel. At 50 °C 1.7131 steel also developed a thin, passive magnetite layer at first, but it quickly dissolved again, and samples stayed grey for the rest of the experiment.

Samples in Table 1 were measured at the start of the experiment (start), after 13 cycles (middle), and at the end after 26 cycles (end). Based on this data, we can assume that 50 °C acid has little effect on the surface of the stainless steel mold, while it significantly worsens mold from the tool steel. Room temperature acid appears not to significantly affect the surface quality of 1.7131 steel mold from values alone, while 80 °C acid will eventually worsen the surface of even stainless steel mold.

Table 1 Surface roughness parameters (Sa and Sz) at the start and end of the measurement

Mat.	Conditions	Sa (μm)	Sz (μm)
M303HH	50 °C start	0.639	5.050
	50 °C middle	0.421	3.334
	50 °C end	0.610	4.879
	80 °C start	0.421	3.788
	80 °C middle	0.458	3.655
	80 °C end	1.011	8.833
1.7131	50 °C start	0.817	6.468
	50 °C middle	1.053	10.050
	50 °C end	3.605	28.177
	RT 23 °C start	0.659	5.249
	RT 23 °C middle	0.713	5.673
	RT 23 °C end	0.609	5.304

Fig. 2 represents a 3D map of the surface of 1.7131 and illustrates the change in roughness parameters. As can be seen, there is a large amount of the individual (up to 14 μm tall) peaks after acid leaching at 50 °C. Acid here likely uncovered individual grain boundaries and preferably dissolved steel at these spots. This is called intergranular corrosion and is highly undesirable. The surface of steel was then less homogeneous, with single grains of steel separated from each other by valleys formed through the loss of regions less resistant than the rest of the alloy. This effect was not observed on stainless steel samples to this degree. Peaks at 80 °C for M303HH reached a maximum of approx. 4 μm .

Surface roughness parameters also do not increase or decrease linearly as can be observed from Table 1. We assume that the cycles of acid preferably attacking grain boundaries, followed by leveling of peaks (grains) were repeated. As grain boundaries are, based on our observations (Fig. 2), weaker to corrosion and therefore lost first, which allows acid to fill in the gaps and quickly remove the rest of the grain providing us the explanation for our findings. However, even with this in mind, the overall trend points out a gradual increase in Sa and Sz at higher acid temperatures where steels are less resistant.

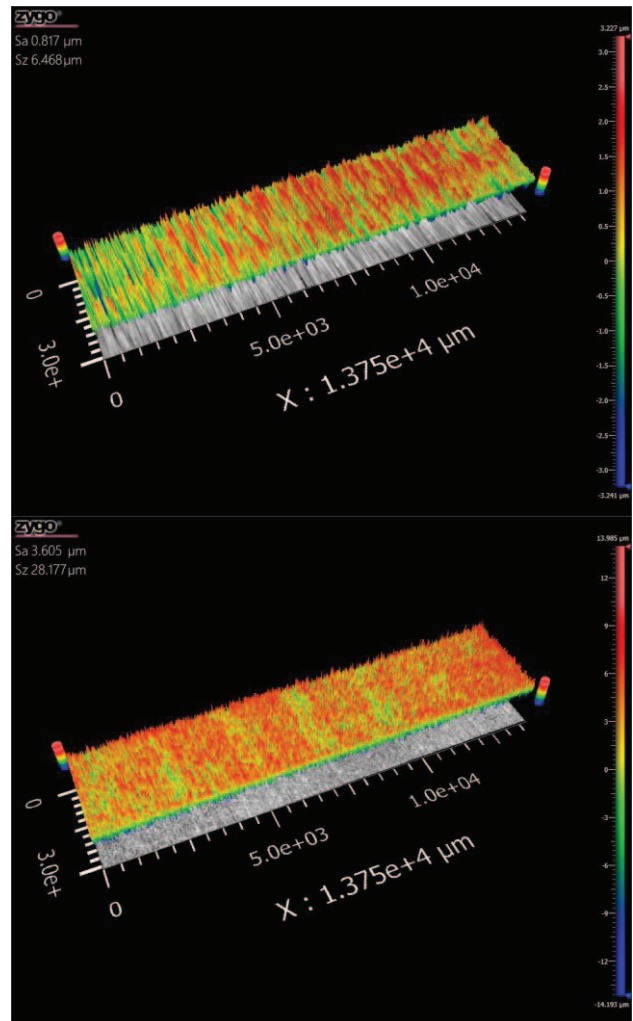


Fig. 2 3D map of roughness parameters of 1.7131 steel, at the start (above) and the end of the experiment (below)

4 Conclusion

This research presents several options for faster and cheaper cleaning of molds from rubber residues. For example, the surface free energy results and consultation with the involved company suggest better results with higher ratios of natural rubber in the compound. This lessens the degree to which rubber sticks to the mold. However, this approach is not feasible for economic reasons. This research direction was therefore abandoned together with attempts to change the MR agent used.

On the other hand, nitric acid showed significantly better results, even at room temperature, in the devulcanization and dissolution of rubber if compared to NaOH currently used in practice. The method utilizing boiling NaOH was nearly completely ineffective for the used compounds. It led to the loss of only approx. 0.3 % of its initial mass

after 24 h, while even room temperature acid led to the loss of 10.8 % after this time. For full disintegration of the rubber, loss of approx. 30 % of its mass is required in this case. The use of the NaOH system was therefore recommended to be reevaluated and possibly discontinued.

Corrosion resistance to nitric acid of a new type of molds from stainless steel is excellent at 50 °C and good at 80 °C while molds made from 1.7131 steel are not recommended for a 50 °C acid bath. They can however resist acid at room temperature to a similar degree as stainless steel ones at 80 °C. However, even at higher investigated temperatures, both types of steel can be considered resistant to corrosion. As this resistance is considered for 1 year of use in the company, we can recommend the use of Nitric acid instead of NaOH for companies using similar cleaning methods. As room temperature acid is much better in dissolving the vulcanized rubber than NaOH, 50 °C should be used only when necessary for molds from 1.7131 and likely other, non-stainless, steels. The use of stainless steel molds, preferably at lower temperatures, is highly recommended for this type of cleaning if a very long lifespan (50+ years) of molds and low maintenance is required.

A comparative study with benzoyl-peroxide is highly recommended, as in practice many common methods, such as laser or dry ice cleaning, have significant disadvantages, for example, high levels of noise. This study can also serve as the basis for further studies utilizing different concentrations and temperatures of acid.

Nitric acid cleaning showed it can be a cheap alternative method, where applicable, as it is near noise-less and technologically simple solution for small companies.

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Contribution of individual authors to the creation of a scientific article (ghostwriting policy)

Martin Novák was responsible for experimental setup, part of corrosion and solubility experiments, and manuscript writing.

Adam Škrobák took part in corrosion and solubility experiments, procured material, did adhesion experiments, and created steel samples.

Berenika Hausnerová prepared the final form of the article, took part in editing, and acted as supervisor of the experiment.

Vladimír Pata carried out surface roughness measurements.

Peter Janovský took part in corrosion and solubility experiments, experiment planning, and material procurement.

Barbora Ptošková carried out testing of surface free energy.

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