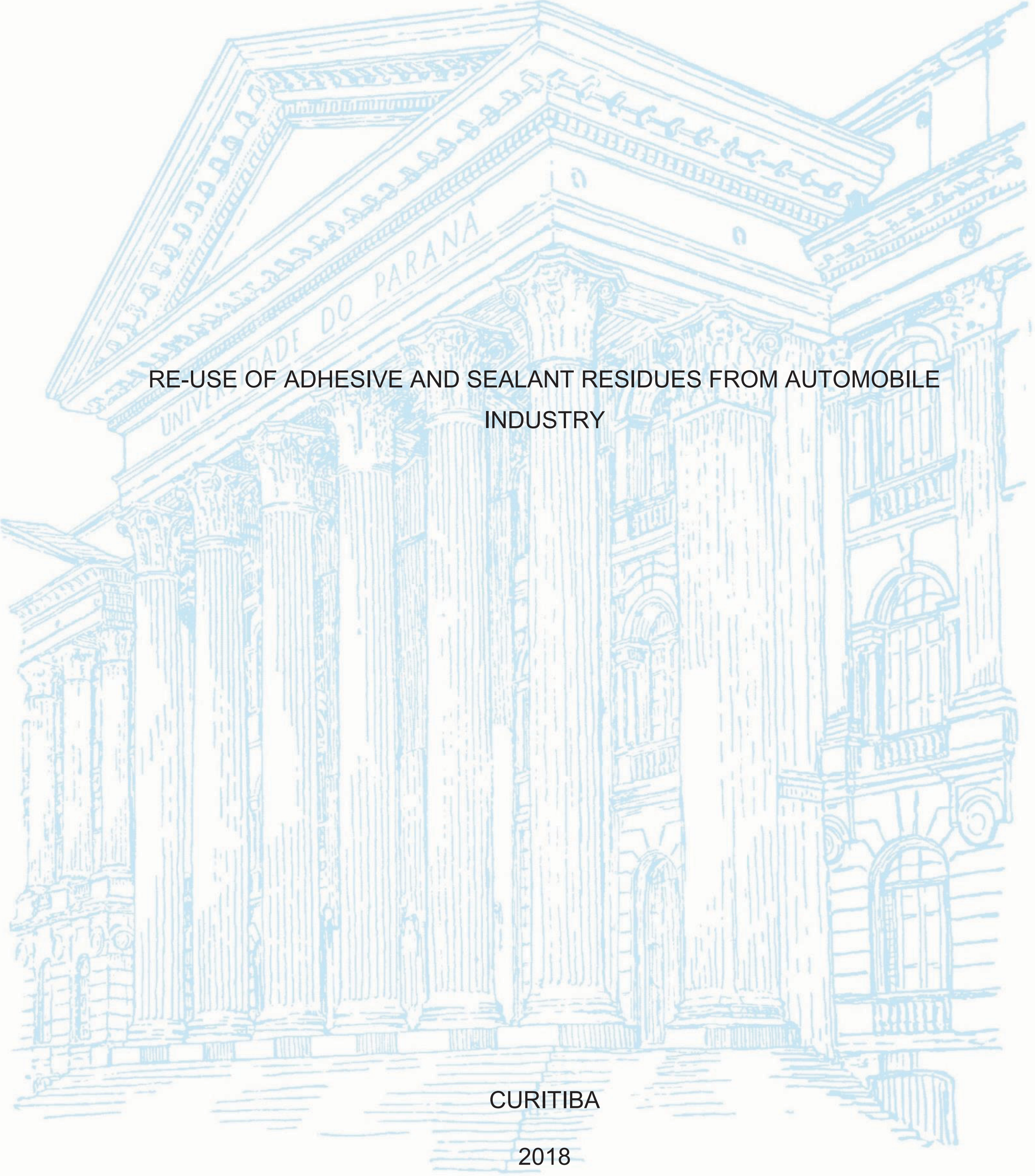
UNIVERSIDADE FEDERAL DO PARANÁ



SIMINDOKHT MOBARAKABADI

RE-USE OF ADHESIVE AND SEALANT RESIDUES FROM AUTOMOBILE INDUSTRY

CURITIBA

2018

SIMINDOKHT MOBARAKABADI

RE-USE OF ADHESIVE AND SEALANT RESIDUES FROM AUTOMOBILE INDUSTRY

Dissertação apresentada ao Programa de Mestrado em Meio Ambiente Urbano e Industrial, Setor de Tecnologia, da Universidade Federal do Paraná e Universidade de Stuttgart e o Sistema Nacional de Aprendizagem Industrial do Paraná, como requisito parcial à obtenção do título de Mestre em Meio Ambiente Urbano e Industrial.

Orientadora: Profa. Dra. . Margarete Casagrande Lass Erbe
Coorientador : Prof. Dipl.-Ing. Matthias Rapf

Dissertation presented to the faculty of Federal University of Paraná, as a partial requirement to obtain the Master's Degree in Urban and Industrial Environment which is a cooperation between the Federal University of Paraná, University of Stuttgart and the National System of Industrial Learning of Paraná.

Advisor: Prof. Dr. Margarete Casagrande Lass Erbe
Co-advisor: Prof. Dipl.-Ing. Matthias Rapf

CURITIBA

2018

FICHA CATALOGRÁFICA ELABORADA PELO SISTEMA DE BIBLIOTECAS/UFPR
BIBLIOTECA DE CIÊNCIA E TECNOLOGIA

M687r Mobarakabadi, Simindokht
Re-use of adhesive and sealant residues from automobile industry / Simindokht Mobarakabadi. – Curitiba, 2018.

Dissertação (Mestrado) - Universidade Federal do Paraná, Setor de Tecnologia, Programa de Pós-Graduação em Meio Ambiente Urbano e Industrial, 2018.

Orientadora: Profa. Dra. Margarete Casagrande Lass Erbe.
Coorientador: Prof. Dr. Matthias Rapf.

1. Gerenciamento de resíduos. 2. Resíduos sólidos industriais. 3. Reciclagem.
I. Universidade Federal do Paraná. II. Erbe, Margarete Casagrande Lass. III. Rapf, Matthias.
IV. Título.

CDD: 628.744

Bibliotecária: Romilda Santos - CRB-9/1214

MINISTÉRIO DA EDUCAÇÃO
SETOR SETOR DE TECNOLOGIA
UNIVERSIDADE FEDERAL DO PARANÁ
PRÓ-REITORIA DE PESQUISA E PÓS-GRADUAÇÃO
PROGRAMA DE PÓS-GRADUAÇÃO MEIO AMBIENTE
URBANO E INDUSTRIAL

TERMO DE APROVAÇÃO

Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em MEIO AMBIENTE URBANO E INDUSTRIAL da Universidade Federal do Paraná foram convocados para realizar a arguição da dissertação de Mestrado de **SIMINDOKHT MOBARAKABADI** intitulada: **RE-USE OF ADHESIVE AND SEALANT RESIDUES FROM AUTOMOBILE INDUSTRY**, após terem inquirido a aluna e realizado a avaliação do trabalho, são de parecer pela sua APROVAÇÃO no rito de defesa.

A outorga do título de mestre está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

Curitiba, 01 de Agosto de 2018.

MARGARETE CASAGRANDE LASS ERBE
Presidente da Banca Examinadora (UFPR)

Rapf
MATTHIAS RAPF
Avaliador Externo (USTUTT)

MARILDA MUNARO
Avaliador Externo (UFPR)

KAmaral
KAREN JULIANA DO AMARAL
Avaliador Interno (UFPR)

"Waste is what remains when you run out of ideas"

-Christian Ekberg

RESUMO

O aumento do consumo de adesivos e selantes na indústria automobilística pode resultar em projetos mais ecológicos, seguindo a política de design mais leve, mas que tem a possibilidade de sobrecarregar o ambiente se houver quaisquer resíduos da aplicação e/ou limpeza. No entanto, ao escolher o plano correto de gerenciamento de resíduos, pode-se reduzir os efeitos adversos do lixo no meio ambiente, economizar recursos naturais e reduzir os custos. No presente estudo, respeitando à política de hierarquia de resíduos, optou-se por avaliar se é possível reutilizar os resíduos de adesivos e selantes não curados gerados por uma indústria automobilística localizada em Curitiba, Brasil, em outros destinos para qualquer produção de bens. Atualmente, a indústria automobilística envia seus resíduos para recuperação de energia em fornos de cimento (coprocessamento). Entretanto, encontrar uma opção de reutilização apresenta vantagens para a proteção ambiental e de recursos. Cumprindo esse objetivo, dois resíduos foram escolhidos para os estudos. Os resíduos foram classificados para avaliar se eram perigosos ou não e caracterizados por meio de análises físico-químicas. A base polimérica foi definida com o auxílio da espectroscopia FTIR. Na etapa seguinte, realizou-se uma pesquisa sobre diversos produtos poliméricos e seu processo de produção, a fim de encontrar destinos que tenham insumos brutos similares, com ingredientes significativos dentro dos resíduos estudados, além de verificar se os resíduos estariam totalmente curados após reutilizados no destino sugerido. Este último fator foi considerado como uma garantia para eliminar possíveis riscos à saúde ou ao meio ambiente que a reutilização dos resíduos poderiam causar. Foi recomendado o reaproveitamento dos resíduos estudados para a produção de produtos como pneus, principalmente pneus poliméricos sólidos; gaxetas de borracha para perfis de portas e janelas; esteiras e pisos; correias transportadoras; correias de transmissão e elevador; revestimento industrial; amortecedores e compósito com matriz polimérica.

Palavras-chave: gerenciamento de resíduos, hierarquia de resíduos, reutilização, resíduos de adesivo, resíduos de selantes.

ABSTRACT

Increasing adhesive and sealant consumption in the automobile industry could result in environmentally friendlier designs by following the lightweight design policy, but it has the possibility to burden the environment if there are residues left over from the application and any cleaning. However, by choosing the right waste management plan, one can reduce the waste's adverse effects on the environment, save the resource and cut down on costs. In the present study, concerning the waste hierarchy policy, it was decided to assess, if it is possible to reuse the uncured adhesive and sealants residues generated by an automobile industry located in Curitiba, Brazil in other destinations for any goods production. At present, the automobile industry sends its residues for energy recovery in cement kilns (co-processing), however considering the waste hierarchy, finding a reuse option is more valuable regarding environmental and resource protection. To fulfill this goal, two residues were chosen for further studies. The physicochemical characteristics of the residues were analyzed to classify the residues and find out their possible hazards. The polymeric base of the residues was defined with the help of FTIR spectroscopy. In the next step, a bibliographic research about various polymeric goods and their production process was done in order to find destinations which have similar raw input materials as the significant ingredients within the studied residues, in addition to the existence of a possibility for the residues to become fully cured after being reused in the suggested destination. The latter factor was considered as a guarantee to eliminate any possible health or environmental risk that reusing the residues may cause. Reuse of the studied residues for production of products such as Tires, especially solid polymeric tires; rubber gaskets for door and window profiles; matting and flooring; conveyor belts; transmission and elevator belts; industrial lining; dampeners, and polymer matrix composite was recommended.

Keywords: waste management, waste hierarchy, reuse, adhesive residue, sealant residue.

ZUSAMMENFASSUNG

Zunehmender Klebstoff- und Dichtstoffverbrauch in der Automobilindustrie könnte zu umweltfreundlicheren Designs führen, indem die Leichtbaupolitik befolgt wird, aber es hat die Möglichkeit, die Umwelt zu belasten, wenn Rückstände von der Anwendung und Reinigung zurückbleiben. Durch die Wahl des richtigen Abfallwirtschaftsplans können jedoch die negativen Auswirkungen des Abfalls auf die Umwelt verringert, die Ressourcen geschont und die Kosten reduziert werden. In der vorliegenden Arbeit wurde in Bezug auf die Politik der Abfallhierarchie entschieden, ob es möglich ist, die ungehärteten Kleb- und Dichtstoffrückstände, die von einer Automobilindustrie in Curitiba, Brasilien, an anderen Bestimmungsorten für die Herstellung von Waren erzeugt werden, wiederzuverwenden. Gegenwärtig schickt die Automobilindustrie ihre Rückstände zur Energierückgewinnung in Zementöfen als Erzatsbrennstoffe, aber unter Berücksichtigung der Abfallhierarchie ist es für den Umwelt- und Ressourcenschutz wertvoller, eine Wiederverwendungsoption zu finden. Um dieses Ziel zu erreichen, wurden zwei Rückstände für weitere Studien ausgewählt. Die physikochemischen Eigenschaften der Rückstände wurden analysiert, um die Rückstände zu klassifizieren und ihre möglichen Gefahren herauszufinden. Die polymere Base der Rückstände wurde mit Hilfe der FTIR-Spektroskopie definiert. Im nächsten Schritt wurde eine bibliographische Untersuchung über verschiedene polymere Güter und ihren Herstellungsprozess durchgeführt, um Optionen zu finden, die ähnliche Rohmaterialien wie die signifikanten Inhaltsstoffe innerhalb der untersuchten Rückstände aufweisen, zusätzlich zu der Möglichkeit für die Rückstände werden nach der Wiederverwendung im vorgeschlagenen Ziel vollständig geheilt. Der letztgenannte Faktor wurde als Garantie dafür angesehen, dass alle möglichen Gesundheits- oder Umweltrisiken ausgeschlossen werden, die durch die Wiederverwendung der Rückstände entstehen können. Wiederverwendung der untersuchten Rückstände zur Herstellung von Produkten wie Reifen, insbesondere festen Polymerreifen; Gummidichtungen für Tür- und Fensterprofile; Matten und Bodenbeläge; Förderbänder; Getriebe- und Elevatorriemen; Industrielles Futter; Dämpfer und Polymer Matrix Composite wurde empfohlen.

Schlüsselwörter: Abfallwirtschaft, Abfallhierarchie, Wiederverwendung, Kleberrückstande, Dichtungsmittelrückstande.

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ABNT	- Associação Brasileira de Normas Técnicas (The Brazilian Association of Technical Standards)
ABS	- Acrylonitrile Butadiene Styrene
EPDM	- Ethylene Propylene Diene Monomer
EVA	- Ethylenevinylacetate
FTIR	- Fourier transform infrared
HMA	- Hot Mixed Asphalt
IMHE	- Industrial Material Handling Equipment
MBTS	- MercaptoBenzThiazole disulfide
NPCS	- Niir Project Consultancy Services
NR	- Natural Rubber
PLA	- Polylactic acid
PMC	- Polymer Matrix Composite
PUR	- polyurethane
PVA	- PolyVinyl Acetate
PVC	- PolyVinyl Chloride
RTV	- Room Temperature Vulcanizing
SBR	- Styrene Butadiene Rubber
SDS	- Safety Data Sheet
TDS	- Technical Data Sheet
TPE	- ThermoPlastic Elastomer
TOC	- Total Organic Content

SUMMARY

1 INTRODUCTION

Adhesives and sealants are applied in a large number of applications in motor vehicles ranging from sports cars to heavy trucks. Beyond traditional applications, such as windshields, brake shoes and thread lockers, adhesives are now being used in applications that were once the exclusive domain of thermal and mechanical joining methods, including the frame, body, dashboard, engine and weather stripping. The market of automotive adhesive and sealant is growing fast. There are several reasons for this trend such as growing rate of plastic and composite consumption in cars and trucks production, which cannot attach them by mechanical fasteners, and the simplification of assembly processes. For instance, parts that are bonded together do not need holes to be drilled or punched, and assemblers do not need to measure torque or double-check fastening operations. Reduction in vehicle weight due to the elimination of fasteners, which is important for automakers trying to maximize fuel economy. The fuel economy regulations, vehicles safety standards and regulations, and increasing focus on the usage of lightweight materials have been counted as reasons why there is a significant increase in this market (HERMANN, 2010; SPROVIERI, 2007).

On the other hand, a variety of adhesives and sealants have been used by the automobile industry. This fact emphasizes the importance of paying more attention to the lifecycle of these materials. The principle of recyclable design will be important in the future. Adhesives as a whole do not represent a major environmental problem, but the impact can be reduced by improving procedures and reducing the use of solvents. Nevertheless, cured and non-recyclable residues, as well as excess adhesive from applications, are waste materials. These materials not only have to be disposed of but also represent an unnecessary use of materials and resources (PACKHAM, 2014).

In the waste management process, according to the waste hierarchy which was introduced for the first time in 1975 by the European union’s waste framework directive (1975/442/EEC) into European waste policy and turned into the present five-step waste hierarchy in 2008, it is recommended in the first place to prevent or minimize the use of materials, and in the second place reuse waste materials before any recycling, recovery or disposal (EUROPEAN COMMISSION, 2008). This aspect is also presented in the Brazilian national solid waste policy, Law N^o 12,305 enacted in 2010. The present study has been developed to find an alternative solution for sealant and adhesive residues generated in an automobile industry, to meet the goal of waste hierarchy as well as the financial benefits of the company.

For the time being, the studied automobile producer sends its residues for co-processing in cement industry. These materials serve as a fuel with high calorific value in the cement kilns; from an environmental point of view, it reduces the waste to landfill by energy recovery, but it is worth to have a better look at the situation and consider that these materials still have utilization potential as they are mostly the leftovers of adhesives and sealants which are not cured. Hence, different options for better waste management based on waste hierarchy will be reviewed in the present study. The main focus will be on ascertaining the possibility of reusing these leftover materials and suggesting the possible destinations in case of having the possibility of reuse.

The motivation behind this research arose from the difficulties that a waste management company located in Curitiba, Brazil, is facing regarding co-processing of uncured adhesive and sealant residues. This company cooperates with different industries and sends the high calorific value solid, liquid or pasty wastes for co-processing in cement industry. The pasty uncured adhesive and sealant residues which are generated in the studied automobile industry, have an adherent nature, which makes the waste handling and conditioning process for co-processing hard. Therefore, this waste management company is not willing to accept these pasty uncured adhesive and sealant materials for co-processing. On the other hand, it is not reasonable to burn a material which is still clean and untouched and has the utilization potential. Moreover, it is possible to cut down on the cost of disposing of still viable materials. Therefore, seeking an alternative destination that can make use of these materials became an important goal for the researcher.

The presented study is a case study and a quantitative methodology is applied during this research. In order to describe the case, the involved units in this study are introduced in a short manner with a description of their activities, and their size. Moreover, the key problems and issues in the case study are identified.

The first involved unit in this study is the automobile industry which generates the adhesive and sealant residues. This factory is located in São José dos Pinhais the metropolitan area of Curitiba, Paraná, Brazil. The plant has a total area of 1.3 million m², of which 305 thousand m² are of built area with about 3,600 employees and four different motor vehicle production. The unit follows the culture of environmental sustainability in its activities and production (VOLKSWAGEN, 2018). The plant have shown an achievement in reduction of waste disposal to industrial landfills by 80% in the first five months of 2016, compared to the same period of 2015 (VOLKSWAGEN, 2016), and continue supporting any idea that help the company walks through the environmental and sustainable pass. Therefore finding a more environmentally friendly sound destination for uncured adhesive and sealant residues which make use of the martial according to priority introduced in waste hierarchy was supported by this industry. During this work, the studied automobile industry will be mentioned as industry A.

The second involved unit is the waste management company which is responsible for receiving the adhesive and sealant residues generated by industry A, in addition to other industrial wastes which are suitable for co-processing. The waste management company which will be mentioned in this work as company B, presents itself as a secure and definitive solution for the final environmentally appropriate disposal of waste, through the technology of co-processing. The company works in partnership with two main cement industries in the area of Paraná state, Brazil; and provide services including environmental licensing, management, transport logistics and operational activities (Pre-conditioning / mixing and co-processing itself). However, the waste valorization is part of their activities as well (REVALORE, 2018).

The case study started with the request of company B. it was mentioned by the company B that they have difficulty for handling and pre-conditioning of the pasty residues generated from uncured adhesive and sealant materials. Moreover, it seems that more value could be dedicated to these residues. Therefore they asked if it is possible to reuse these residues in processes like road construction (asphalt).

Consequently, the study began with the idea to assess the possibility of reusing the uncured adhesive and sealant residues generated in industry A, in other destinations.

1.1 OBJECTIVES

1.1.1 General Objective

Finding an alternative destination which can reuse the uncured adhesive and sealant residues generated by the automobile industry.

1.1.2 Specific Objectives

- Choose the most abundant residue which has a pasty characteristic as the main focus of study.
- Classify the chosen residue with help of Brazilian norms.
- Identify the main polymeric base of chosen residue in order to find the reuse possibilities base on its polymeric characteristics.
- Select the best destinations which can reuse the residue.

2 REVIEW OF THE LITERATURE

In order to become familiar with the topic and the materials which are studied in this work, some terms need to be defined. Therefore in the literature review some basic terms regarding the polymers and some of the applications for different polymeric materials which are considered to be related to the study is provided in the following.

2.1 ADHESIVES AND SEALANTS

Adhesives and sealants are mostly made of similar materials, and they can be used in similar applications as well (PETRIE, 2007). Hence, adhesives and sealants are most of the times considered together. However, different specifications and test methods apply to adhesives and sealants, and most often they are used to perform different tasks. The adhesive and sealant definitions indicate these different functions, and according to PETRIE these definitions are (2007, p. 3):

> Adhesive—a substance capable of holding at least two surfaces together in a strong and permanent manner.
>
> Sealant—a substance capable of attaching to at least two surfaces, thereby, filling the space between them to provide a barrier or protective coating (PETRIE, 2007, p. 3).

Adhesives can have natural or synthetic origin. The TABLE 1 shows the classification of adhesives based on their origin.

TABLE 1- ORIGIN, BASIC TYPE, AND CHEMICAL FAMILY OF COMMON ADHESIVES

(To be continued)

Origin	Basic type	Family	Examples
Natural	Animal	Albumin Animal glue Casein Shellac Beeswax	

(To be continued)

Origin	**Basic type**	**Family**	**Examples**
	Vegetable	Natural resins	Gum Arabic, tragacanth, colophony, Canada balsam
		Oils and waxes	Carnauba wax, linseed oil
		Proteins	Soybean
		Carbohydrates	Starch, dextrins
	Mineral	Inorganic minerals	Silicates, magnesia, phosphates, litharge, sulfur
		Mineral waxes	Paraffin
		Mineral resins	Amber
		Bitumen	Asphalt
Synthetic	Elastomers	Natural rubber	Natural rubber and derivatives
		Synthetic rubber	Butyl, polyisobutylene, polybutadiene blends, polyisoprenes, polychloroprene, polyurethane, silicone, polysulfide, polyolefins
		Reclaimed rubber	
	Thermoplastic	Cellulose derivatives	Acetate, acetate-butyrate, caprate, nitrate, methyl cellulose, hydroxyl ethyl cellulose, ethyl cellulose, carboxy methyl cellulose
		Vinyl polymers and copolymers	Polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride
		Polyesters (saturated)	Polystyrene, polyamides
		Polyacrylates	Methacrylate and acrylate polymers, cyanoacrylates
		Polyethers	Polyhydroxy ether, polyphenolic ethers
		Polysulfones	

(Ending)

	Thermosetting	Amino plastics Epoxies	Urea and melamine formaldehydes epoxy polyamide, epoxy bitumen, epoxy polysulfide, epoxy nylon
		Phenolic resins and modification	Phenol and resorcinol formaldehydes, phenolic-nitrile, phenolic-neoprene, phenolic-epoxy
		Polyesters(unsaturated)	
		Polyaromatics	Polyimide, polybenzimidazole, Polyphenylene
		Furanes	Phenol furfural

SOURCE: PETRIE (2007).

Alongside, also sealants can be originated from organic or synthetic materials. Generally, sealants contain inert filler material and are usually formulated with an elastomer to give the required flexibility and elongation. Asphalt, bitumen, oleoresinous, butyl, hypalon, ethylene propylene diene monomer (EPDM), neoprene, styrene-butadiene, polyvinyl chloride, acrylic solution, acrylic emulsion, polyvinyl acetate, polysulfide, polyurethane, silicone, fluoropolymers, epoxies and intumescents are the main materials which can appear as the base of a sealant (PETRIE, 2007).

In the first place any adhesive or sealant should be in the form of liquid or paste with relatively low viscosity that has the ability to wet the substrate’s surface at joint. On the other hand most of the sealed or adhesive joints carry some mechanical loads, however it is resulted from the weight of the substrates or it is the purpose of joint to be able to transfer mechanical loads efficiently from one to another substrate. For an adhesive or a sealant to fulfill these criteria, once it established interfacial contact i.e. completely wet the substrate, it must then harden, set or cured (KINLOCH, 1990). In the present study the hardened adhesive will be called as cured adhesive.

There are many ways to classify adhesives and sealants, such as by bonding mechanism, chemistry type, and even application (e.g. structural vs. non-structural), however the methods by which the adhesives may transform from a liquid or paste state to a solid state (hardening, curing, or setting process) are more related to this study. The hardening of adhesives can be accomplished in several ways such as: by solvent or dispersing medium removal, by cooling (hot-melt adhesive with thermoplastic polymeric base), and by chemical reactions (one-part thermoset adhesives, two-part adhesives, anaerobic adhesives, etc.). In addition, there are those adhesives which are an exception to this classification and do not undergo hardening (pressure-sensitive adhesives) (KINLOCH, 1990).

On the other hand, many different adhesives, sealants, and coating compounds with various properties, from high-strength structural adhesives with energy-absorbing properties (crash resistance) to surface-coating compounds with high elasticity, are used in modern automobile manufacturing. The transition between adhesives and sealants is not defined precisely. In modern automobile manufacturing, the increasing in automation and the use of robots for body assembly led to high adhesive and sealant consumption. Mostly, it is preferred to use one-component formulations with wash-off resistance that are cured by the heat of the electro coat, primer, and paint bake ovens. In the other sections of manufacturing, where no bake ovens are available, mainly one-component, moisture-curing, or contact adhesives are used, and two-component products are used mainly to bond plastics (HERMANN, 2010; KLOSOWSKI, 2017).

In the presented study, the focus is on the material used in the body shop. The types of adhesives and sealants used in the body shop are heat-curable and the purpose of using these materials is the assembly of car’s metal structure. Bond sealers, anti-flutter, hem-flange, and structural adhesives are the most used materials in this section (MERZ el at., 2008).

2.2 THERMOSETS VERSUS THERMOPLASTICS

Polymeric materials are classified, based on the recycling or reprocessing of the material into two groups: “Thermoplastic polymeric materials” or “Thermoset polymeric materials” (SUBRAMANIAN, 2014).

Thermoplastic polymeric material is a plastic material which has the ability to become pliable or moldable in a specific elevated temperature. There is no chemical reaction taking place during this heating. The material remains in the plastic state as long as the temperature is maintained and solidifies upon cooling. Thermoplastic polymers are processed in the molten state without altering their molecular structure. Acrylic, acrylonitrile butadiene styrene (ABS), nylon, polylactic acid (PLA), polybenzimidazole, polycarbonate, polyether sulfone, polyoxymethylene, polyetherether ketone, polyetherimide, polyethylene, polyphenylene oxide, polyphenylene sulfide, polypropylene, polystyrene, polyvinyl chloride, and teflon are classified as thermoplastics (SUBRAMANIAN, 2014).

Thermoset polymeric material is a plastic which undergo chemical reactions to irreversibly cure from a soft solid or viscous liquid prepolymer or resin to an infusible, indissoluble and crosslinked product. Among thermosets, epoxy resins are the best-knowns, others include phenolic resins, unsaturated polyesters, polyurethanes, dicyanates, bismaleimides, silicone resins, acrylates and methacrylates (GOTRO et al., 2017).

For many applications, designers can combine the two materials to take advantage of the best features each material have to offer. Understanding the unique qualities of each material can help designers and engineers make well-informed decisions about product design and material selection (SIMTEC, 2016).

For instance a two-component injection molding, combine thermoset and thermoplastic materials. With these kinds of techniques, it is possible to design more complex parts, improve product quality and material bonding, and reduce the costs and assembly time. The key for a successful result in these methods is the right combination of materials. The designer must factor in the shrinkage difference between the two materials, and the thermoplastic must have the thermal capability within the temperature range which the thermoset cures (SIMTEC, 2016). BEX et al. (2018) considered the “wetting measurements as a tool to predict the thermoplastic/thermoset rubber compatibility” as well. It is proved that the wetting behavior of a molten thermoplastic on a thermoset substrate is an essential step in the formation of a strong interface (BEX, 2018).

Moreover, there are many thermosets which are modified with thermoplastic materials. These modifications affect morphology and mechanical properties of one brittle thermoset polymer. The toughening mechanisms include cavitation, shear banding, bridging, crack pinning, crack blunting, etc. (KIM, 2005). During past decades many efforts were devoted to improve the toughness of thermosets, especially epoxy resins among others. Dispersion of elastomeric and thermoplastic phases into the resin matrix is considered as the most successful strategies regarding the toughening of epoxy resins, which leads to a multiphase polymeric system (QIN et al., 2003).

2.2.1 Thermoset Adhesives

Both thermoset and thermoplastic polymeric materials have been used for production of adhesives and sealants. However the residues in this study are generated from thermoset adhesives, therefore having a short description about this type of materials is important.

A thermoset adhesive is an adhesive which transforms from liquid or pasty state to a solid state (harden, cure, or set) by chemical reactions in elevated temperatures. The term cured is used when some form of chemical reaction takes place within the adhesive or sealant. This chemical reaction is called “polymerization”, “cross-linking” or “curing” and cause the constituents like monomers or oligomers join up to become larger molecules (polymers). The polymerization mechanisms are divided into two groups, the step-growth (condensation) polymerization and additional polymerization which take place in three distinct steps: initiation, propagation, and termination. It is not possible that one adhesive cure by itself. There is always a way to trigger the necessary reactions to start the curing process. There are basically three ways for curing:

(1). one way is to mix two or more components together. These type of adhesives are called ‘two-part’ adhesives. The mixing of two parts, the ‘resin’ and ‘hardener’, causes the cure. The speed of curing can be anything from a few minutes to some hours. In industrial applications, two-part structural adhesives are usually based on epoxy, methacrylate or polyurethane (KINLOCH, 1990).

(2). in other formulations, the polymerization may only trigger at elevated temperatures. These types of adhesives are ‘one-part’ formulations. The type of the materials has been studied during this research fall into this category. However, the curing process occurs in elevated temperatures, but it is possible that some chemical reactions start at room temperature before application of adhesive on substrates, hence the limited lifetime of these type of adhesives is the reason why the automotive industries are so strict on using adhesives which the packages are left open for a while or they are out of specific storage environment (KINLOCH, 1990).

(3). in some cases, the chemical reactions in ‘one-part’ formulated adhesives may proceed at room temperature when the reactions catalyzed by an external source such as Ultraviolet light, the absence of oxygen and presence of metal ions like the anaerobic adhesives, or the presence of moisture with example of cyanoacrylates, Room-Temperature-Vulcanizing (RTV) silicones or Urethanes (KINLOCH, 1990).

The thermoset adhesive is a one or two-part adhesive which is cured when exposed to specific temperatures for a specific period of time. The rigid polymeric network structure of the thermoset adhesive which is formed during curing process is responsible for the physical and chemical properties of it. Thermoset adhesives show some distinguishing properties like infusibility, insolubility in various media, high load-bearing ability, and high creep resistance. They show high compatibility in extreme service conditions like exposure to salt water, radiations, or performing well in high and low temperatures. Gradually the thermoset adhesives are replaced with traditional joining methods due to their exceptional properties which led to lightweight constructions. The main thermoset adhesives are based on epoxy resins, cyanoacrylates, and polyurethanes (ENGELS, 2018).

2.2.2 Polymeric Materials (Thermosets/Thermoplastics) and Composite Manufacturing

It is not just adhesives and sealants that are consist of polymeric materials. There are many different applications for polymeric materials (thermosets/thermoplastics) and among them the composite manufacturing. The composite manufacturing is a vast field in the area of applied science and manufacturing which provides the possibility of using a variable polymeric materials. Therefore a short overview on the composite science and the processes which the polymeric materials can be used in composite manufacturing is provided. These pieces of information provide a general impression about the final destinations which use polymeric material in their activities and products, and can be a possible destination for the uncured adhesive and sealant residues with a polymeric base.

According to the composite definition, it is a material made from two or more distinct materials with significantly different physical or chemical properties that, when they are combined, a material with characteristics different from the individual is formed. This combination basically improves product performance and/or lower production costs. However, the term composite has developed to mean a material containing a “matrix” or base substance and a “reinforcement” material. The matrix could be polymer, metal, ceramic, or carbon which provides the bulk form of the product, holds the imbedded phase in place, and shares the load with the secondary phase, and the reinforcement material in form of fiber, particle, flake, etc. serves to strengthen the composite (HOA, 2018; MIDDLETON, 2018).

The composite materials are classified in three groups: metal matrix composites, ceramic matrix composites, and polymer matrix composites. A polymer matrix composite (PMC) is a composite consists of a polymer matrix imbedded with reinforcing phase such as fibers or powders. Generally, in PMC’s manufacturing, there are many different material options to choose from in the areas of resins, fibers and cores, all with their own sole set of properties like toughness, strength, stiffness, heat resistance, production rate, cost etc. Though, the final properties of a composite made from these diverse materials do not only depend on the individual properties of the resin matrix and fiber (and in sandwich structures, the core as well), but is also a function of the way in which the materials themselves are designed into the part and also the way in which they are processed (HOA, 2018; MIDDLETON, 2016).

More information about the polymeric matrix materials and a set of the most commonly used composite production methods are presented in following. This information could help to assess if this industry could be a possible destination for the studied residues reuse.

2.2.2.1. The matrix

Presence of the matrix material is necessary for binding the fiber reinforcement, giving the composite component its shape and determines the composite surface’s quality. A matrix can be polymeric, ceramic or metallic or carbon; and polymeric matrices are the most widely used for composites.

In the polymer matrix composite materials, there are thermosetting resin-based composite materials and thermoplastic resin-based composite materials, as well as one-component polymer matrix composite materials and polymer blends matrix composite materials. However, thermosets are among the most widely used materials. Unsaturated polyester resins, epoxy resins, phenolic resins, cyanate esters, and polybutadiene resins are some examples of the most used thermoset resins. On the other hand, polyethylene, polyethylene terephthalate, polybutylene terephthalate, polycarbonate, acrylonitrile butadiene styrene, polyamide and polypropylene with lower cost and limited use temperatures, and polyetherketone, polyamide-imide, polyarylsulfone, polyetherimide, polyethersulfone, polyphenylene sulfide and liquid crystal polymer with high-performance and higher costs are among the thermoplastic resins have been used in composite manufacturing (WANG et al., 2011).

Many studies have been developed in the field of composites. Among them what interest this study more, is the developments regarding natural rubber application for composite manufacturing (FLINK et al., 1990; SUI et al., 2008; MENTE et al., 2016; JACOB JOHN et al., 2008; NAIR et al., 2014); since this fact indicates the possibility of reusing the uncured rubber-modified thermoset adhesive and sealant residues.

2.2.2.2. Composite Manufacturing Methods

There are numerous methods for manufacturing composite components. Composite fabrication processes include some form of molding, to shape the resin and reinforcement. A mold tool is required to give the shapeless resin /fiber combination its shape prior to and during cure.

There are various shaping processes for a composite manufacturing. The shaping methods used to produce composites include: Open molding (which consist either hand layup or a semi-automated alternative, spray up), Resin infusion processes (including resin transfer molding, resin injection molding, vacuum-assisted resin transfer molding, and resin film infusion), and High-volume molding methods (such as compression molding, injection molding, filament winding, pultrusion, tube rolling, automated fiber placement, automated tape laying, and centrifugal casting) (BRAVO et al., 2017; SME, 2018).

Thermal curing is a critical step in manufacturing composite materials. Several curing methods are available. Curing process can happen by applying heat, typically with an oven, and pressure, by means of a vacuum. Many high-performance thermoset parts require heat and high consolidation pressure to cure. In order to provide this conditions, the use of an autoclave is required. Moreover, Electron-beam (E-beam) curing has been explored as an efficient curing method for thin laminates (SME, 2018).

2.3 RUBBER ELASTOMERS

The other term which is important to be defined is rubber elastomers; since the studied materials in this work are adhesives and sealants which contain rubber as a modifier in their formulation. Therefore having a short introduction about the rubbers and their applications would be helpful. There are many different kinds of rubbers, but they all fall into two wide-ranging types: natural rubber (NR) and synthetic rubber.

A natural rubber is an elastomer made from milky white liquid called latex. It consists of polymers of the organic compound isoprene also known as 2-methyl beta-1,3-diene with the chemical formulation of ($C5H8$)n, slight impurities of other organic compounds, and some water (CHARLES et al., 2003).

A synthetic rubber is any artificial elastomer which is made in chemical plants using petrochemicals as its starting point. Commercially, the most important synthetic rubbers are styrene butadiene (SBR), polyacrylics, and polyvinyl acetate (PVA); polychloroprene (better known as neoprene), and various types of polyurethane (CHARLES et al., 2003).

The term elastomer stands for a material that shows rubbery properties (i.e. that can recover most of its original dimensions after extension or compression). Polymer chains are held together in these materials by relatively weak intermolecular bonds, which permit the polymers to stretch in response to macroscopic stresses. When elastomers are extended or stretched, the individual long-chain molecules are partially uncoiled but will retract when the force is removed (MORTON, 2009).

Elastomers are normally thermoset (requiring vulcanization) but there are also some thermoplastic forms of elastomers. The long polymer chains cross-link during curing (i.e. vulcanizing). For instance, natural latex rubber is easy to pull apart since there many weakly linked long polymer molecules existing in the material. When natural rubber is cooked with sulfur, the sulfur atoms form additional cross-links, locking the molecules together and making them much harder to pull apart. This process is called vulcanization and it results in the strong, durable, rubber (PIELICHOWSKI et al., 2013).

There are many applications for rubbers depending on each rubber product. Natural rubber, polybutadiene, ethylene propylene diene monomer, Styrene Butadiene rubber, butyl rubber, nitrile butadiene rubber, and chloroprene rubber are among the most used rubbers (BRENTIN et al., 2011). For instance, the various applications of the natural rubber are reviewed in following. These variable applications indicate the possibility of using each rubber in various destinations:

(1) Tires: Regardless of the competition of synthetic compounds, natural rubber continues to keep its importance in tire consumption. In passenger car cross-ply tires, natural rubber is used in the carcass because of its good tear resistance, building tack, and ply adhesion. In radial ply tires, natural rubber is also commonly used in the sidewalls due to its lower heat generation and well fatigue resistance. In the treads of passenger car tires in the United States, Western Europe, and Japan, virtually no natural rubber is used, except in winter tires. In large truck and off-the-road tires, which require low heat generation and high cutting resistance, almost 100% natural rubber is used (BRENTIN et al., 2011).

(2) Industrial and Consumer Goods: Industrial applications cover a variety of products such as conveyor belts, transmission and elevator belts, industrial lining, hoses and tubes, and rubberized fabrics. NR is also used in consumer products such as rubber bands, pencil erasers, sporting goods (e.g. golf or football balls), footwear or other clothing (BRENTIN et al., 2011).

(3) Engineering Products: Engineering applications include parts such as bridge bearing pads, seismic bearing pads, dock fenders, springs, anti-vibration mountings and vehicle suspension systems. In this part, the high mechanical strength and low creep under load are vital properties as well as the good heat build-up properties. As other important uses of rubber one can mention gaskets for door and window profiles, matting, flooring, and dampeners (BRENTIN et al., 2011).

(4) Other: Other end uses include objects for use in the health sector (particularly condoms, catheters and surgical gloves) and latex articles such as threads, adhesives, and molded foams. Toy balloons are also large consumers of concentrated latex. They are also used as an adhesive in many manufacturing industries and products (BRENTIN et al., 2011).

In the present study, the natural rubber have been used as modifier in the formulation of adhesives and sealants which the studied residues are generated from. This is the reason why among all kinds of rubbers just different applications of natural rubber is provided. Moreover, among all of these applications, some are explained in more detail in the following. This is for bringing more information about each product's manufacturing process and specification related to the product. Each sub-section is related to a final destination that it is estimated to be potential for accepting the studied residue for reuse.

2.3.1 Rubber-Resin Blends and Rubber-Based Adhesives

There are numerous adhesives consist of rubbers and resins, both natural and synthetic, which obtain combinations of both types of materials' properties and characteristics. Depend on the type of rubber and resin used in rubber-resin blends and their ratio; the blended adhesive can be applied in structural or general purpose bonding. For instance, thermosetting resins modified with synthetic rubber are used for the structural bonding of metal and other rigid materials. Phenolic-nitrile and phenolic-neoprene adhesives are examples of this type, where the rubber improves the pliability of bond and its resistance to any shock or impact. Rubber-resin adhesives are available in form of structural and non-structural adhesives. The structural rubber-resin adhesives normally cure at elevated temperatures about 180-200°C and a pressure ranging between 30-100 N/cm^2. The non-structural rubber-resin adhesives are normally hardening by solvent or dispersing medium removal as they are mostly supplied as solutions in an organic solvent (NPCS, 2008).

Natural Rubber and neoprene, Butyl Rubber and Polyisobutylene, Nitrile Rubber, Styrene-Butadiene, and thermoplastic Rubbers are the most common types of rubbers that are used in rubber-base adhesives formulation (MARTÍNEZ, 2002).

Natural rubber adhesives are commonly employed to bond non-metallic materials such as leather, fabrics, paper, and other rubber products. Natural rubber adhesive formulations are heavily modified with synthetic resins and additives in order to obtain tailored properties. Natural rubber and neoprene are said to have similar properties but neoprene is known to form stronger bonds and shows good resistance to heat and aging. On the other hand, natural rubber adhesives show good resistance to water, but poor resistance to oils, organic solvents, and chemical oxidizing agents. The long tack retention properties of natural rubber have made it ideal for pressure sensitive adhesive formulations (KHAN, 2011). Several synthetic rubber are used as raw materials for adhesives and sealants as well. Amongst them are polychloroprene, styrene butadiene, nitrile, and polyisobutylene rubber. (SKEIST, 1990).

Rubber base adhesives in most cases contain an elastomer and a tackifying or modifying resin as the main components, but in addition to these main components other ingredients are also included. In the formulation of rubber base adhesives many additives such as plasticizers, softeners, fillers, pigments, curing agents, antioxidants, solvents, emulsifiers, coagulants, biocides, etc. can be found. It is not necessary to use all these ingredients in formulation. There are some general aspects related to the formulation of rubber base adhesives. Depending on the type of adhesive and its properties different additives are used. For instance, in solvent-borne rubber adhesives, a variety of solvents can be chosen to control drying rate, adjust viscosity and dissolve important ingredients. Resins can be added to improve tack, wetting properties, heat resistance, bond strength and oxidation resistance. Plasticizers and softeners decrease hardness, improve tack and reduce cost of rubber adhesive formulations. Fillers are not commonly added to rubber adhesive formulations as they decrease adhesion; however they reduce cost and increase solution viscosity. As an instance carbon black filler is used to give reinforcing effect and in case of natural rubber to act as a chromophore (light-absorbing additive) to inhibit chemical reactions that lead to rubber degradation. In water-borne adhesives, protective colloid, preservative, de-foamers, wetting agents and emulsifiers are included in the formulations as well (MARTÍNEZ, 2002).

2.3.2 Tire Manufacturing

There are many industries that make use of tires in their manufacturing. Pneumatic tires are used as a part of many types of vehicles, including cars, bicycles, motorcycles, buses, trucks, heavy equipment, and aircraft. On the other hand, the solid rubber (or other polymers) tires are also used in various non-automotive applications. Casters, carts, lawnmowers, and wheelbarrows are examples of this type of solid tires. Following are some detail information regarding the specifications and manufacturing process of tire products.

2.3.2.1. Pneumatic tires

Complex product engineering is needed in case of a passenger car, lorry, and off-the-road tires production. They consist of many different rubber compounds, various types of carbon black, fillers like clay and silica, and some chemicals and minerals. Moreover, several types of fabric for reinforcement and many kinds of steels which vary in type and size is used during manufacturing of tires. Some of these steels are twisted or braided into strong cables (EVANS, 2006). TABLE 2, illustrates the composition of a tire.

TABLE 2- COMPOSITION OF A TIRE.

Ingredient	**Passenger car tire**	**Lorry tire**	**Off-the-road tires**
Rubber/Elastomers	∀[1]47%	∀45%	∀47%
Carbon Black	∀21.5%	∀22%	∀22%
Metal	∀16.5%	∀25%	∀12%
Textile	∀5.5%	-----	∀10%
Zinc oxide	∀1%	∀2%	∀2%
Sulphur	∀1%	∀1%	∀1%
Additives	∀7.5%	∀5%	∀6%
Carbon-based materials, total	∀74%	∀67%	∀76%

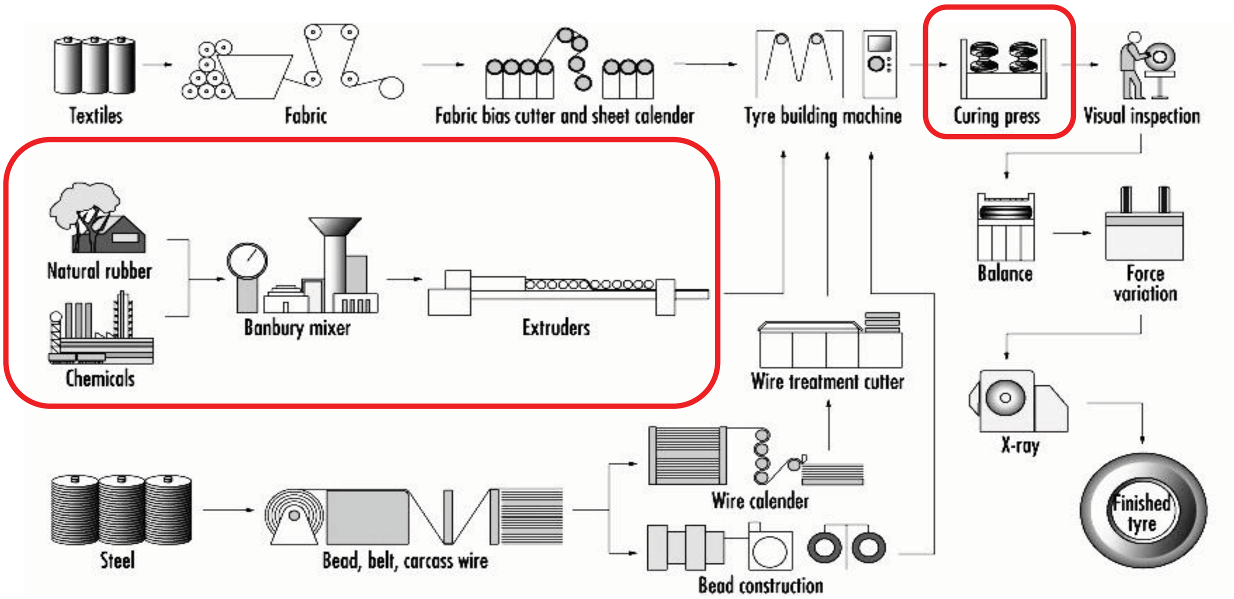
[1] The upside-down A symbol is the universal quantifier from predicate logic. It means that the stated assertions holds "for all instances" of the given variable.

SOURCE: EVANS (2006).

In addition to the information have been provided in TABLE 2, lorry and off-the-road tires are normally contained higher proportions of natural rubber than passenger car tires. Moreover, some of the additives include clays, may be replaced in part with recycled rubber crumb from waste tires, and in this case, the approximate carbon-based materials existing in the tire would be slightly higher. According to EVANS (2006), a common-sized all season passenger car tire, on average, weighing about 10 kg and it contains: 30 kinds of synthetic rubber; 8 kinds of natural rubber; 8 kinds of carbon black; Steel cord for belts; Polyester and nylon fiber; Steel bead wire; and 40 different chemicals, waxes, oils, pigments, silica, and clays.

Basic steps in pneumatic tire manufacturing process are chemical mixing, material processing (calendaring, extruding, making beads), tire building and curing process. FIGURE 1 illustrates schematically the process of pneumatic tire manufacturing.

FIGURE 1 -PROCESS OF PNEUMATIC TYRE MANUFACTURING



SOURCE: BANDARA (2011).

In the first step of tire manufacturing, the raw materials are mixed according to the recipe of each particular tire. The raw materials and their percentage vary depending on the need of the customer and the performance of the tire. However, the main raw materials used for tire manufacturing are natural rubber, synthetic rubber, a carbon filler, and chemical additives. The output of this step is called “rubber compound” (BANDARA, 2011).

Afterward, the rubber compound has to undergo several processing operations to become suitable for tire building. This step is called material processing. Inner liner calendaring, for making inner layer of tubeless tires; fabric calendaring process, for covering the rubber layers on both side; a separate steel wire coating operation for making steel beads; and a rubber extrusion process to extrude outer layer (tread) of the tire are the steps in the material processing section (BANDARA, 2011).

The output of the material processing step is sent to the tire building machine. The operator of the tire building machine winds the plies on an expanded or collapse drum of building machine according to the specified tire construction. It is basically started with inner liner, several plies from rubber coated fabric, then two bead rings at the two edges and finally the thread on the top. The final output of this section is called “green tire” (BANDARA, 2011).

Later the green tire is sent to the painting stage. At this stage the outside and inside of the green tire is painted according to the requirements. Inside paint is acting as lubricant between green tire and the curing bladder. Outside paint is acting as an agent to increase the flow properties of the tread (BANDARA, 2011).

Next stage is the tire curing process. In this phase, the green tire is placed over a bladder which is attached in the center of the tire mold. Mold has connected to a curing press heated platen. Steam is used to heat up the curing press platen. Firstly apply pre-shaping steam pressure into the bladder and then close the mold and apply high-pressure steam into the bladder. Subsequently, the curing bladder pushes the green tire into the mold. Due to the heated mold and bladder inside steam heat, the green tire starts to vulcanize. Generally, it takes 30 to 60 minutes to cure a tire but it can vary depending on the tire’s dimension and compounds. During the curing process, green tire takes the shape of the mold and the lug pattern. In the end, the produced tire is sent to the quality inspection section to check whether its quality meets the required level or not (BANDARA, 2011).

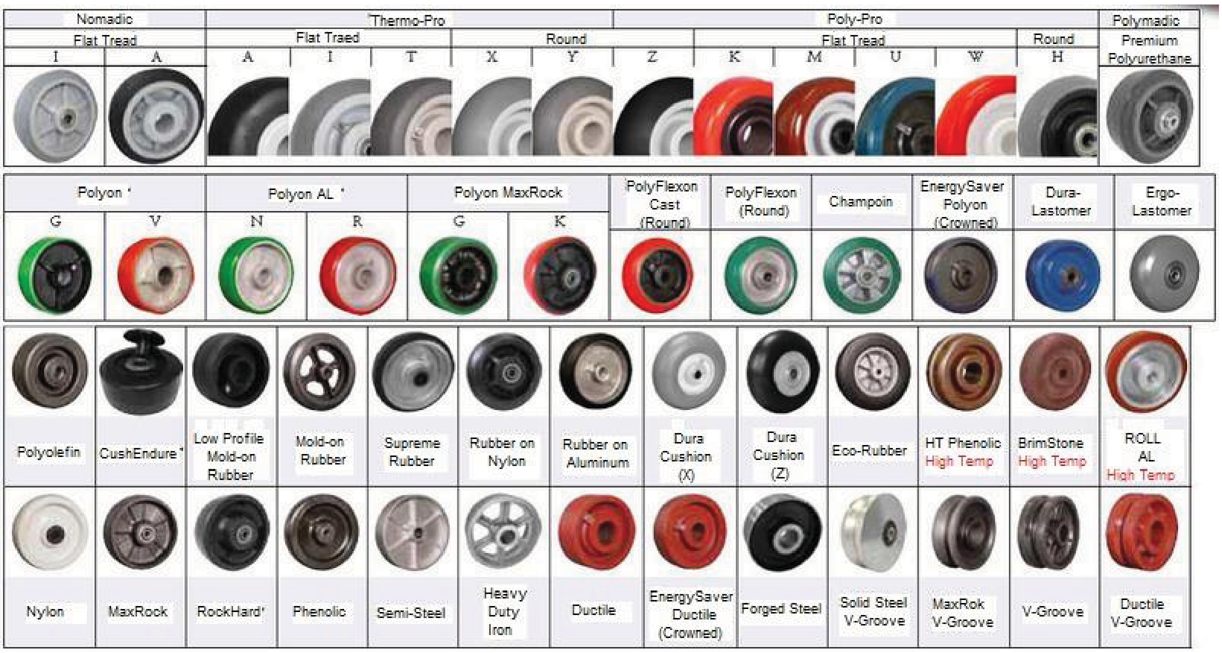
Among all these steps, two are more related to the present work and are center of the attention. These two steps are shown in the FIGURE 1, with a circle around the process. In the first place the raw polymeric materials, elastomers and different additives are mixed during the tire manufacturing process. This step is the place which may have the possibility to accept the studied residues as an input to be mixed with other raw input materials. And the existence of a curing step can guarantee that the added uncured thermoset adhesive and sealant residues will be cured during this process.

2.3.2.2. Solid Tires

Solid tires have been used in a variety of applications. From large tractors and trucks to the smaller equipment such as Forklifts, even smaller applications including bike tires, lawnmower tires, or casters all contain solid tires (RIGHTTURN, 2018).

Solid rubber tires are used in various non-automotive applications. An example of this category could be the rubber tires which are made for casters. Casters are found almost everywhere, from office desk chairs to shipyards, from hospital beds to automotive factories. They vary in size and individual load capacities. Depending on the floor type, condition, and cleanliness and the expected duty that casters need to fulfill, they can be made of various materials. Wheel materials include cast iron, plastic, rubber, polyurethane, forged steel, stainless steel, aluminum, and more (BC, 2018). FIGURE 2 illustrates the different types of caster tires.

FIGURE 2- DIFFERENT TYPES OF CASTER TIRES



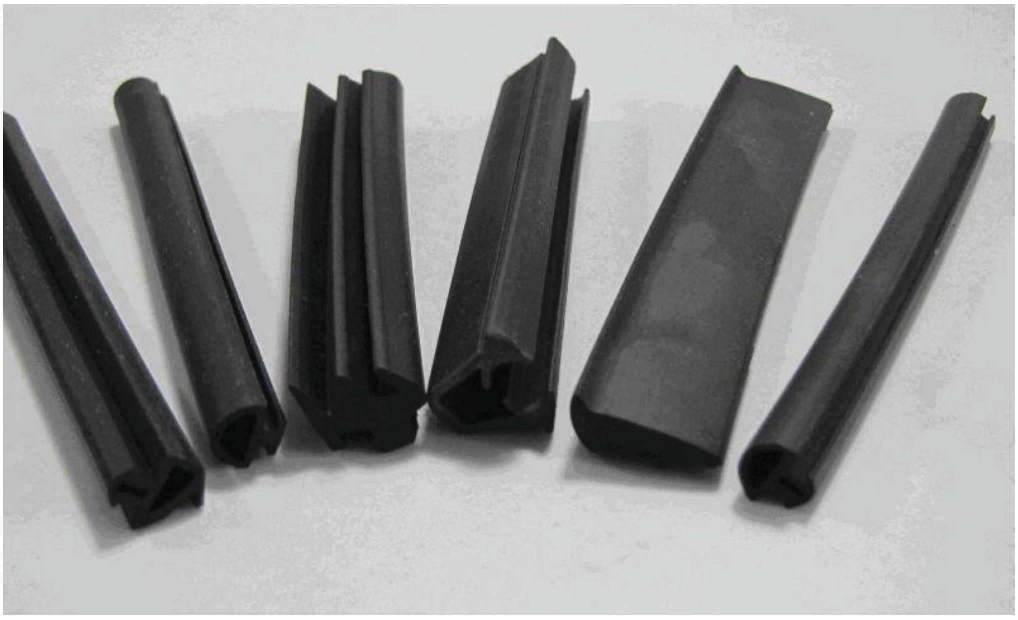
SOURCE: adapted from IMHE (2018).

An elastic natural rubber caster Wheel manufacturing is an example of the potential destination that has the possibility to use the uncured rubber-based adhesive and sealant residues. The standard elastic natural rubber caster Wheel is normally produced from a mixture of natural rubber (NR) and Styrene butadiene rubber (SBR). Some fillers, chemicals, and additives also must be blended with this mixture in order to provide the required properties of the rubber caster, such as tensile strength, wear resistance and flexibility. The principal ingredients of a rubber mixture included around 50-60% raw rubber, Carbon Black Particles, and various chemicals to provide resistance to ozone and sunlight. In addition to assisting the materials processing and manufacturing method oil may be used to help process the material, and also Sulphur which is employed to vulcanize the rubber mixture, After the substances have been produced it is ready to be utilized for the molding process (BC, 2018).

2.3.3 Gasket for door and window profiles

A variety of different materials have been used for the manufacturing of door and window profile's gaskets depending on the customers' need. EPDM, Chloroprene (Neoprene), silicone, nitrile, natural rubber, SBR, fluoroelastomers, thermoplastic elastomers (TPE), and flexible PVC are among the materials which have been used depending on the desired application and performance. For instance, a natural rubber gasket offers high tensile strength, good friction surface, and strong resilience properties, in addition to resistance to organic acids and alcohols. Also, it has high tear-resistance properties with excellent adhesion to metal surfaces. The ability to absorb vibration makes natural rubber ideal for use as dampeners. FIGURE 3 shows the different configuration of a door and window gasket (KRP, 2018).

FIGURE 3- DOOR AND WINDOW PROFILE GASKET

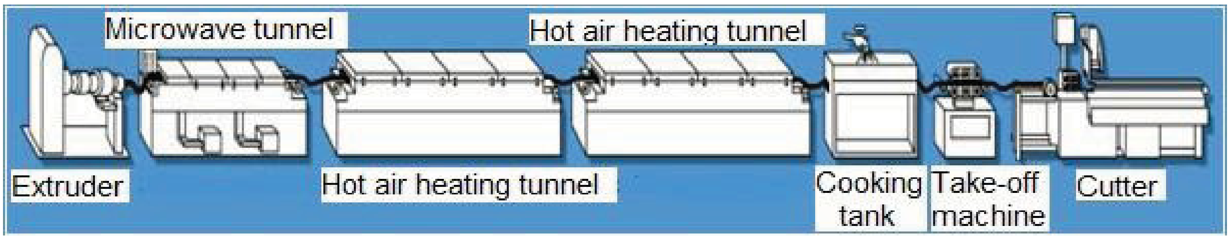


SOURCE: KRP (2018).

A rubber extrusion process applies in order to make the rubber gaskets for door and window profiles. Rubber extrusion does not differ so much from plastic extrusion. Mainly, the major difference is the curing process or vulcanization of the rubber during the extrusion process. During the extrusion process, the rubber is forced through a die of the favorite cross-section under pressure from an extruder. Formerly, the rubber part must be vulcanized before it would be ready to use. The processes of vulcanization or curing take place during the last step of the extrusion process. This helps the rubber extruded profiles to preserve its shape and gain the essential physical properties (KRP, 2018; CROWTHER, 1998).

Various types of rubber extrusion processes exist. Among them, it is possible to mention: (1) Continuous in-line cure extrusion: The rubber material moves through a curving tunnel that elevates the product to the proper vulcanizing temperature (CROWTHER, 1998). Figure 4 illustrates a continuous cure extrusion process. (2) Off-line cure extrusion: The warm rubber is driven through the die and then exposed to high-pressure steam in order to reach the suitable vulcanizing temperature (CROWTHER, 1998).

FIGURE 4- RUBBER'S CONTINUS CURE EXTRUSION PROCESS



SOURCE: adapted from CROWTHER (1998).

2.3.4 Rubber matting and flooring

There is a great variety of materials have been used for manufacturing mats. In general, raw materials for the manufacturing of rubber floor mats include various kinds of rubber, including natural rubber, nitrile rubber, styrene-butadiene rubber etc. in addition to vulcanizing agents, colorants, stabilizers and other necessary additives (NWB, 2018).

Moreover, the process of rubber floor mats production is not a complicated process. In the first place, the rubber is mixed inside the kneader or any other mixing device with stabilizers, vulcanizing agents, forming agents, and pigments to make compounded rubber. In the next step, the compounded rubber is shaped in the form of a sheet in the proper thickness, width, and length. Finally, this sheet is placed in a mold and heated in the hydraulic press to get vulcanized. After the curing time, the cured rubber is taken out and trimmed to get the final product (NWB, 2018).

2.4 ROAD CONSTRUCTION, USING THE RESIDUES IN ASPHALT

As the study began with the question of company B, regarding the possibility of using the uncured adhesive and sealant residues in asphalt, having an overview about this destination would be useful. In this section a short description of asphalt characteristics and composition is provided. An introduction to modified asphalt is presented in order to open the research gate for farther investigations on the possibility of using the rubber-based residues in asphalt formulation as a modifier.

2.4.1 Asphalt Composition

The hot-mixed asphalt (HMA) which is used for constructing the surface layer of asphalt concrete pavements consists of two main parts: asphalt binder, and aggregates, and in some cases, some chemical additives can be added to modified asphalt formulations. ‘Asphalt binder’ is a blend of hydrocarbons of different molecular weights, and it is the product of the distillation of crude oil. ‘Aggregate’ is a collective term for the material derived from natural rocks such as sand, gravel, and crushed stone. Aggregates are an important ingredient of the materials used in road construction. Up to 75-85% of HMA’s volume consists of aggregate, and the physical, mechanical, and chemical properties of the aggregate play an important role in the performance of an asphalt concrete pavement. The ‘chemical additives’ are usually used to enhance the mixture resistance to some pavement distresses, such as moisture susceptibility, rutting, or fatigue cracking (PAPAGIANNAKIS et al., 2012).

2.4.2 Asphalt binder

Chemical Composition of Asphalt Binder in molecular level, consist of so-called hydrocarbons such as (1) An aliphatic structure of straight or branched chains; (2) an unsaturated ring or aromatic structure; or (3) saturated rings or branches, which have the highest hydrogen-to-carbon ratio. Additionally, asphalt also includes heteroatoms such as nitrogen, sulfur, oxygen, and metals. Although these heteroatoms exist in small percentages compared to the hydrocarbons, they influence the interactions among molecules and asphalt properties (PAPAGIANNAKIS et al., 2012).

There are many properties within an asphalt binder which affect its performance. Viscosity, penetration, dynamic shear, flexural creep, tensile strength, surface energy, and aging are the factors that are studied for evaluation of one asphalt binder. Different methods have been developed over the years for grading asphalt binders. The main objective of these grading systems is to classify binders based on their rheological and mechanical properties, assuming that these properties relate to the field performance. Some of the asphalt grading systems are: (1) penetration grading, (2) viscosity grading, (3) aged residue’s viscosity grading, and (4) Superpave performance grading (PAPAGIANNAKIS et al., 2012).

2.4.3 Modified Asphalts

In modified asphalts, different processes and materials are used to enhance the binder properties. The goal is to increase the maximum and/or reduce the minimum temperature at which a binder can be used. Among the key factors in this field can mention to the increase in traffic loads, new refining technologies, enhancement in polymer technology, the increasing need to recycle waste such as rubber, and the need to meet the performance grades in the Superpave system. Some examples of different kinds of additives can be found in TABLE 3.

TABLE 3- TYPES OF ASPHALT BINDER MODIFIERS

Categories of Modifier	**Examples of Generic Types**
Thermosetting polymers	Epoxy resin Polyurethane resin Acrylic resin
Elastomeric polymers	Natural rubber Volcanized (tyre) rubber Styrene-butadiene-styrene (SBS) block copolymer Styrene-butadiene-rubber (SBR) Ethylene-propylene-diene terpolymer (EPDM) Isobutene-isoprene copolymer (MR)
Thermoplastic polymers	Ethylene vinyl acetate (EVA) Ethylene methyl acrylate (EMA) Ethylene butyl acrylate (EBA) Polyethylene (PE) Polyvinyl chloride (PVC) Polystyrene (PS)
Chemical modifiers and Extenders	Organo-managanese/cobalt compound (Chemrete) Sulphur Lignin
Fibers	Cellulose Alumino-magnesium silicate Glass fiber Asbestos Polyester Polypropylene

Categories of Modifier	**Examples of Generic Types**
Antistripping	Organic amines Amides
Natural binders	Trinidad lake asphalt (TLA) Gilsonite Rock asphalt
Fillers	Carbon black Fly ash Lime Hydrated lime

SOURCE: PAPAGIANNAKIS et al. (2012).

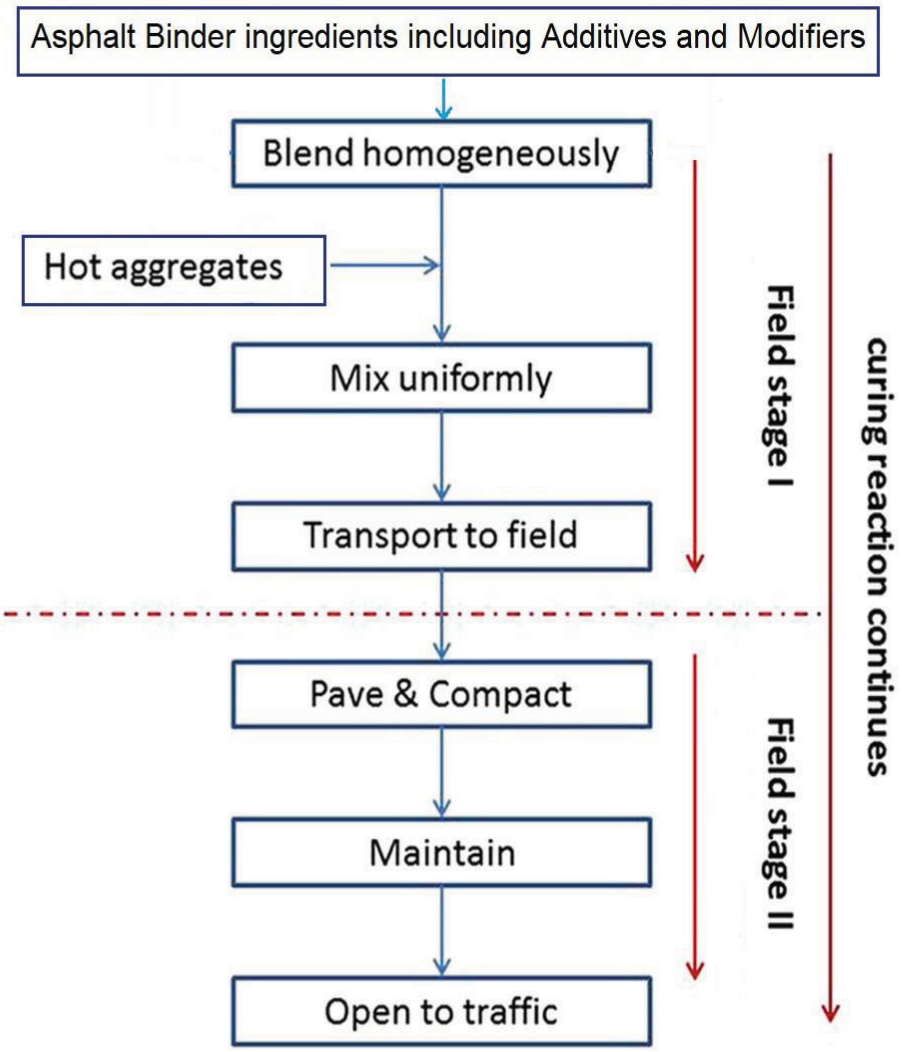
As it is illustrated in TABLE 3, there are many polymeric materials that have been added to the formulation of asphalt. Modified binders are shown more resistance to fatigue, thermal cracking, rutting, stripping, and temperature susceptibility than non-modified binders. Polymer modified binders tend to exhibit increased viscosity and elastic recovery, although penetration does not appear to be influenced by modification (YILDIRIM, 2007). According to King et al. and his colleagues, the results of modifying asphalts depend on a number of factors, such as concentration of the modifiers; molecular weight; chemical composition; particle size; and molecular orientation of the additive, crude source, refining process, and the grade of the original unmodified binder (KING, 2001).

The modification has its own drawbacks since the compatibility between an asphalt and a modifier is not assured, it may result into phase separation during the storage, transportation, application or service which leads to a poorly performing pavement. Moreover, the normal grading systems, especially Superpave performance system, were designed for non-modified binders. These systems are not suitable for polymer modified binders. Since, however, asphalts modified with different polymers can have the same performance grade, but it is observed that they can perform very differently. However, there are new testing methods that have been developed or altered for modified binders include measuring the softening point and elastic recovery, and a force ductility test (YILDIRIM, 2007).

2.4.4 Hot-mixed asphalt preparation and application

On typical HMA applications there are three main parts. Preparation of asphalt binder and aggregate separately and make them ready for mixing, mixing the asphalt binder and aggregate, and paving process. Among these steps what interests this study is the binder preparation where the uncured adhesive and sealant residues may have the possibility to be added; and duration and temperature by which the asphalt binder and aggregates are mixed and prepared for paving, since the temperature and duration of this mixing can have a direct effect on curing of the uncured adhesive and sealant residues. To shorty review the process of HMA preparation and application the FIGURE 5 is provided.

FIGURE 5- THE PROCESS OF HMA PREPRATION AND APPLICATION.



SOURCE: adapted from KANG ET AL. (2016).

As it is mentioned in the FIGURE 5, curing of one thermoset resin or rubber which is added to the binder formulation as a modifier can occur during both field stages I and II. The duration and the temperature in field stage I, where the asphalt binder is mixed with aggregates is one important step. Typically in laboratory environment maintaining longer mixing periods in the desired mixing temperature lead to complete curing, however, at the paving site where the asphalt is exposed to the atmosphere, desired temperatures (in average120-130 °C) would not be maintained for more than a short while during the paving process. Consequently, to achieve a performance that is equivalent to that in the laboratory, sites paved systems should be naturally maintained in a hot summer and stay in rest for a long period before become open to traffic (KANG et al., 2016).

3 METHODOLOGY

The present study is a case study and a quantitative methodology is applied during this research. The project was initiated by the request of a waste management company located in Curitiba, Brazil, and during this project, the possibility of reusing uncured adhesive and sealant residues generated by an automotive industry was assessed.

The data regarding the adhesive and sealant consumption was provided by the studied automobile industry. Moreover, an investigative process was used during this project. A visit from industry was planned on 26. Jan. 2018, in order to investigate the process of waste generation and the situation of the waste storage station. Safety Data Sheet (SDS) and Technical Data Sheet (TDS) of each product used by the industry were reviewed for a better understanding of materials' characteristics. Considering the statement of the waste management company responsible for final waste disposal (TISSOT, 2017), regarding the undesirable adherent characteristic of pasty residues for co-processing; two similar products' residues were chosen as the main focus of study due to their abundance and their pasty structure. Extra physical, chemical, and base polymeric identification tests were undertaken for the chosen residues to find the reuse options according to the residue's physicochemical and polymeric characteristics. Additional information was gathered through a literature review.

Finally, based on the waste material characteristics and the literature review, high potential destinations for reusing the adhesive and sealant residue generated by automobile industry were proposed.

3.1 CHOOSING A RESIDUE AS THE MAIN FOCUS OF STUDY

Considering the limited time and budget allocated to the project, studying all the residues was beyond the scope of this study. Therefore, it was decided to choose a residue as the focus of study.

To choose the main residue for further studies, two criteria were considered to be important and effect on decision making: (1) Abundancy of the residue (2) pasty structure of residue. It is worth mentioning that the pasty structure of residue is just a physical indicator of adherent property of the residue.

The process of choosing was conducted in a way that, in the case of two residues with almost the same generation portion, the one with pasty characteristics is the choice. The reasoning behind this approach is that: firstly, finding a reuse option for the most abundant residue will lead to saving more material by bringing them to lifecycle, and secondly the uncured adhesive and sealant residues with pasty structure are not suitable for co-processing due to their adherent characteristic. For this reason, finding an alternative final disposal option had been requested by the waste management company (TISSOT, 2017).

It was anticipated that the most used materials lead to the most generated residues. In order to prove this anticipation and choose the target residue for further studies, the following steps were taken:

(1). Information reviewing: The information regarding the adhesive and sealant consumption in the studied automobile industry was requested. This information helps to mark the most used adhesive and sealant products by the studied company.
(2). Field observation: In order to prove the anticipation: “the most used products lead to the most generated residues”, a visit to the waste storage station of the studied industry was conducted to find out how much of each product’s residue exists in the waste storage station. In order to fulfill this goal, the numbers of each product’s drums were counted, since the residue of each product is sent to waste storage station in its original drum. Therefore, the number of drums is a good indicator for anticipating the amount of each residue. The results of this observation and survey were presented in form of a percentage of each product’s residue in compare to all adhesive and sealant residues in waste storage station. This methodology was chosen since there is no information recorded on the amount of each residue specifically neither by the automobile industry, nor the waste management company who is responsible for final disposal of these types of residues.
(3). Decision making: Observations of researcher along with all information provided by the industry on the product utilization were recorded. Moreover, a review on the SDS and STD of candidate products with abundance in their residues among others and a pasty structure was conducted. It was decided in case of finding similarities

between these two candidates according to their SDS/TDS, both would be chosen as the focus of study.

3.2 CLASSIFICATION OF CHOSEN RESIDUE

In order to classify a residue, having knowledge about the process or the activity that gave rise to the residue, the residue's constituents, and its characteristics, is necessary. Therefore, to meet this objective the following steps were taken:

(1). Identification of residue generation process: in order to identify the process of residue generation, a visit from production line where the residue is generated, was conducted. Moreover, a visit to the waste storage station was carried out in order to investigate the situation of residue at waste storage. These two steps are necessary in order to check if any possible contamination during the residue generation process, or at waste storage station could infect the residue since the presence of any hazardous contamination would have a direct effect on the classification of a residue.

(2). Collection of samples: two samples from each chosen residue were collected throughout the process of sample collection according to the Brazilian norm ABNT NBR 10007 from the waste storage station in industry A. The sample collection was carried out by the technician of the EP Analítica Laboratory on 02/03/2018. Each sample was collected separately and was labeled with the name of the product and sampling date.

(3). Preparation and analysis of samples: the preparation and analysis of the samples in this study were carried out by EP Analítica Laboratory and the results were presented to the researcher.

(4). Consulting with Brazilian norm ABNT NBR 10004 regarding final classification: After receiving the results of flammability, solubility, and leachability tests, the results were compared to the limits which are published in Brazilian norm ABNT NBR 10004. By following the norm steps regarding the classification of solid waste, the studied residues were classified.

3.3 IDENTIFYING THE MAIN POLYMERIC BASE OF CHOSEN RESIDUE

In order to find any compatibility between the residue and the final reuse option, knowing the ingredient presented in the residue is necessary, but it is known that identification of the polymeric base of any adhesive and sealant product is a hard and complicated procedure and in many cases impossible. It needs using the full array of available analytical instrumentation such as Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Surface Analysis methods such as Scanning Electron Microscopy (SEM) or Energy Dispersive X-ray Analysis (EDXA), and physical/thermal testing such as Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Dynamic Mechanical Analysis (DMA). It is clear that an innovative manufacturer which develops a polymer-based product should be sure that it is not possible for the competitors to reverse engineer his products. Therefore, in the presented study it is decided to use the simplest and the most economical method, FTIR spectroscopy, just in order to make a comparison between the existing spectrums in the databases and the spectrum resulted from the analyzed sample. This comparison leads the researcher to indicate the presence of the main ingredients within the sample. The following steps show the approach which was made towards this methodology:

(1). the measurements were made in Transmittance mode with 32 scans and 4cm^{-1} resolution.
(2). the results were compared with the database of © 2014 NICODOM.
(3). the main ingredients were identified.

3.4 DESTINATION FOR REUSE

The methodology behind this section covered a comprehensive bibliographic research in addition to the consulting with the polymer engineers who work in different manufacturing sections.

In the first step in order to answer to the question, whether it is possible to use the studied residues as an additive to asphalt or not, the researcher reviewed the previous articles and data on modified asphalts to assess whether technically it is a possible solution or not. In the next step, a review on environmental safety aspects was performed in order to assess the possibility of reusing the residues in applications such as asphalt that provides a direct contact between the residues and the environment.

In general, every new waste which is suggested for use as secondary material must be tested on its equality to the original input material in the suggested destination and its environmental safety. In the next step, In order to suggest some final destinations for reuse of the studied residues, these two factors were considered important:

1. The existence of a similarity between the raw input materials of the chosen destination and the significant ingredients within the studied residues. This factor is a start point for introducing the residues to the final destinations. To fulfill this goal, all the information had been gathered through this study regarding the identification of residues' ingredients were reviewed, however, the result of polymeric base identification was the most important information which the researcher based her suggestions on it in order to propose the possible reuse destinations. Moreover, among the possible destinations, the ones which present less risk to human health and the environment were chosen.

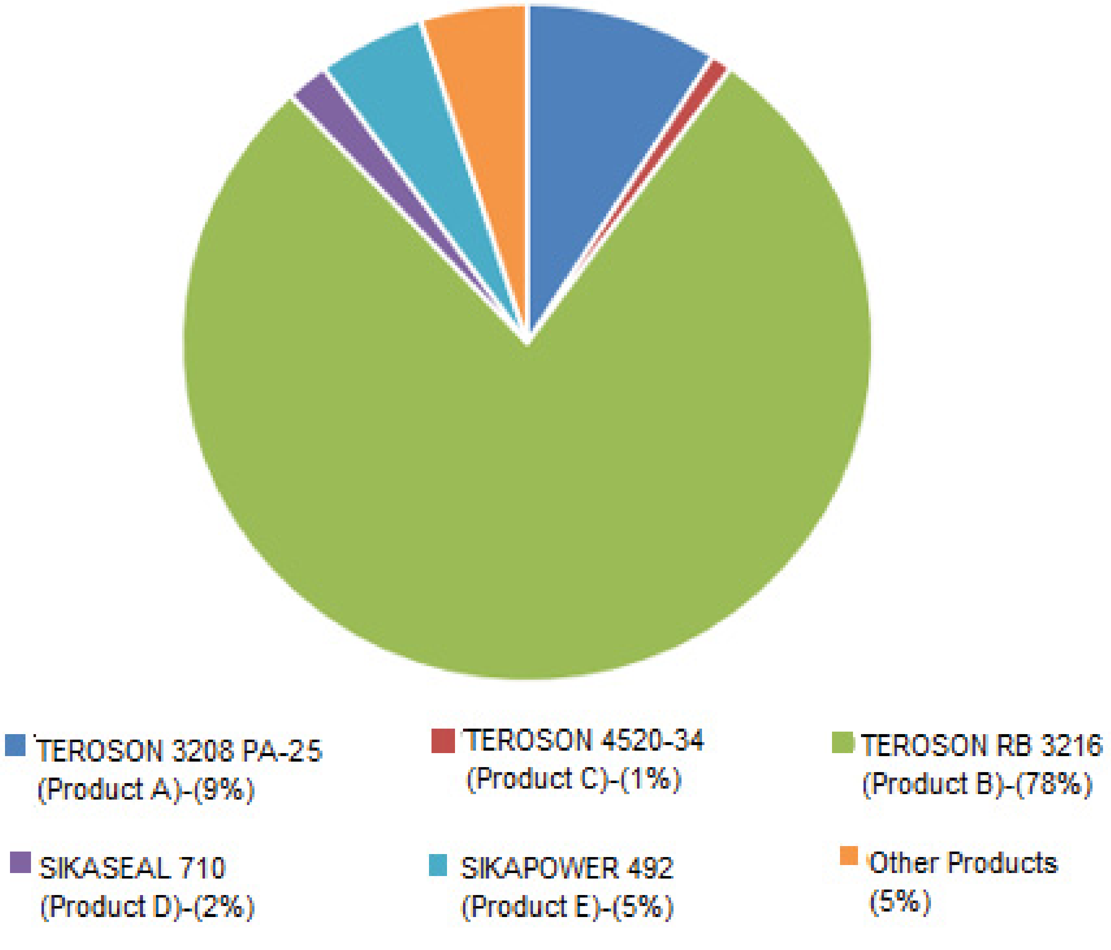
2. The existence of the possibility for the residues to become fully cured after being reused in the suggested destination. This factor is to assure that reusing the residue will not cause any environmental risk. In general, completely cured adhesives and sealants could be regarded as non-toxic and safe materials (YANG et al., 2015). Therefore, the manufacturing process of industrial products, which have the factor one criteria (The existence of a similarity between the raw input materials of the chosen destination and the significant ingredients within the studied residues) was reviewed. The destinations which provide the possibility of being fully cured to the residues were chosen as the final destinations.

4 RESULTS

4.1 CHOSEN RESIDUE

A list of the most used adhesive and sealant products by the industry A (an automobile producer factory located in São Jose dos Pinhais – PR) were provided to the researcher. The following are the most frequently used products which are illustrated in FIGURE 6 schematically by the percentage.

FIGURE 6- ADHESIVE AND SEALANT CONSUMPTION IN THE INDUSTRY A



SOURCE: adapted from THE INFORMATION PROVIDED BY THE “INDUSTRY A” (2017).

As it is shown in FIGURE 6, the Product B in the first place and Product A in the second place form the most significant portion of the utilized products among the other adhesive and sealants. As a result, it was anticipated that residues which are generated by the industry A, would show the same result with the highest generated portion in Products B and A.

The results after the researcher's observation during the visit from waste storage station of the studied automobile industry are provided in the form of a table. The amount of each residue is provided in the form of percentage in comparison with other existing residues in the waste storage station on the date which the visit had been held. TABLE 4, presents the information about the existing residues in the waste storage station.

TABLE 4- RESIDUES' INFORMATION

Residue	Original Product which the Residue is Generated from	Residue's Physical Appearance*	Residue's Quantity*
Residue I	TEROSON RB 3208 PA-25	Pasty[1]	16%
Residue II	TEROSON RB 3216	Pasty	10%
Residue III	SIKAPOWER 492	Solid	36%
Residue IV	SIKAFLEX- 250MKV-3	Pasty	4%
Residue V	TEROSON RB 3255 VW-25	Pasty	4%
Residue VI	BETAMATE^{TM} 1480V203	Pasty	4%

* Information on residues quantity and appearance has been provided based on the observation of the author on the sampling date.

SOURCE: THE AUTHOR (2018).

According to the TABLE 4, the main residues are originated from Product E (SIKAPOWER 492), Product A (TEROSON RB 3208 PA-25), and Product B (TEROSON RB 3216); and all residues have pasty characteristics except the Residue III which is in the solid state.

A comparison between the information about the residues (TABLE 4) and the information that was provided by the industry A on the product consumption of the factory (FIGURE 6) shows, however, the Product B has the most consumption portion, but it does not lead to higher residue production. Product E with total use of 5% has

---

[1] A pasty material is a material which resembling paste in consistency.

the highest amount of residue (Residue III) in the waste storage station. And the second major portion of residues generated from Product A.

The reason behind this fact is explainable by the process that industry applies the product. The automatic application system that applies Product E on the substrates is designed to support big drums of adhesives and sealants, while this product consumption is low. Therefore, the high quantity of raw material remains unused in each drum after running the application device. Although the visit showed that this material has the most abundant portion among residues, but it would not be a suitable choice as the focus of study, because in this study it is decided to look for residues with pasty characteristics and this residue is in the solid state. Moreover, it was mentioned by the production technician of the studied automobile industry that factory started to replace Product A with Product B in some sectors and this fact resulted in more residue production of this product.

According to the fact that Product A is replaced with Product B in some sections of the production line (SILVA NETO, 2018), it was decided to gather more information regarding these two products and compare their SDS and TDS together to have a better understanding about their safety aspects and Technical applications. Moreover, it is worth to mention that the characteristics of each product can be valid for the residues which are generated from that mentioned product with really close estimation. Since the residues that are studied in this work are leftovers from an application process without undergoing any curing or hardening process (it is explained in detail in section 4.2.1). This is the curing process that changes the characteristics of an uncured adhesive or sealant (KINLOCH, 1990), and as long as the adhesive or sealant did not undergo a curing process, a major change in the characteristic of the material would not be expected.

TABLE 5 and 6 are illustrating a short comparison between the environmental and personal safety consideration and technical information on Product B and Product A.

TABLE 5- “PRODUCT A” ENVIRONMENTAL AND PERSONAL SAFETY AND TECHNICAL CONSIDERATIONS.

Product Name	**Environmental Safety Aspects**	**Personal Safety Aspects**	**Technical Aspects**
TEROSON RB 3208 PA-25	**Anti-flutter Adhesive- Rubber Technology**		
	-Classification N- Dangerous for the environment R51 / 53- Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. **-Safety Phrases** S57- Use appropriate containment to avoid environmental contamination. S61- Avoid release to the environment. Refer to special instructions/safety data sheets. **-Hazardous components which cause acute toxicity** 2,2-Dibenzothiazyl Disulfide Phthalic Anhydride Zinc oxide **-Qualitative solubility** (20°C (68 ° F), Solvent: water): insoluble	**-Classification** R36/37/38- Irritating to eyes, respiratory system and skin. R31- Contact with acids liberates toxic gas H317- May cause an allergic skin reaction. H334- May cause allergy or asthma symptoms or breathing difficulties when inhaled. **-Safety Phrases** S51- Use only in well-ventilated areas. S38 - In case of insufficient ventilation wear suitable respiratory equipment. S36- Wear suitable protective clothing. S37 - Wear suitable gloves. S39- Wear eye/face protection. -**Hazardous components which irritate skin, eye and respiratory system** Calcium oxide 2,2-Dibenzothiazyl Disulfide Phthalic Anhydride C,C'-azodi (formamide)	-Heat Curing -Solvent-free -One component adhesive -Rubber-based -Flexible bonding, the cured materials shows a foamy structure which is highly flexible and little dependent on temperature change. -Compatible for adhering to oily steel sheets, aluminum, and zinc coated surfaces. -Chemically cross-links at temperatures above 140°C. -Application temperature is between 35 to 60°C. -Curing condition: 25 min. at 175°C. -Paintable

SOURCE: adapted from SAFETY AND TECHNICAL DATA SHEET OF TEROSON RB 3208 PA-25 (2018).

TABLE 6- “PRODUCT B” ENVIRONMENTAL AND PERSONAL SAFETY AND TECHNICAL CONSIDERATIONS.

Product Name	Environmental Safety Aspects	Personal Safety Aspects	Technical Aspects
TEROSON **RB 3216**	**Anti-flutter Adhesive- Rubber Technology**		
	-Classification N- Dangerous for the environment R50 / 53- Very toxic to aquatic organisms may cause long-term adverse effects in the aquatic environment. **-Safety Phrases** S57- Use appropriate containment to avoid environmental contamination. S61- Avoid release to the environment. Refer to special instructions/safety data sheets. **-Hazardous components which cause acute toxicity** 2,2-Dibenzothiazyl Disulfide Zinc oxide **-Qualitative solubility** (20°C (68 ° F), Solvent: water): insoluble	**-Classification** R36/37/38- Irritating to eyes, respiratory system, and skin. H317- May cause an allergic skin reaction. H334- May cause allergy or asthma symptoms or breathing difficulties when inhaled. R3 - Contact with acids liberates toxic gas. **-Safety Phrases** S51- Use only in well-ventilated areas. S38 - In case of insufficient ventilation wear suitable respiratory equipment. S36- Wear suitable protective clothing. S37 - Wear suitable gloves. S39- Wear eye/face protection. **-Hazardous components which irritate skin, eye and respiratory system** Calcium oxide Sulfur	-Heat Curing -Solvent-free -One component adhesive -Rubber-based -Flexible bonding, the cured materials shows a foamy structure which is highly flexible and little dependent on temperature change. -Compatible for adhering to oily steel sheets, aluminum, and zinc coated surfaces. -Chemically cross-links at temperatures above 140°C. -Application temperature is between 35 to 60°C. -Curing condition: 25 min. at 175°C. -Paintable

SOURCE: adapted from SAFETY AND TECHNICAL DATA SHEET BY AUTHOR (2018).

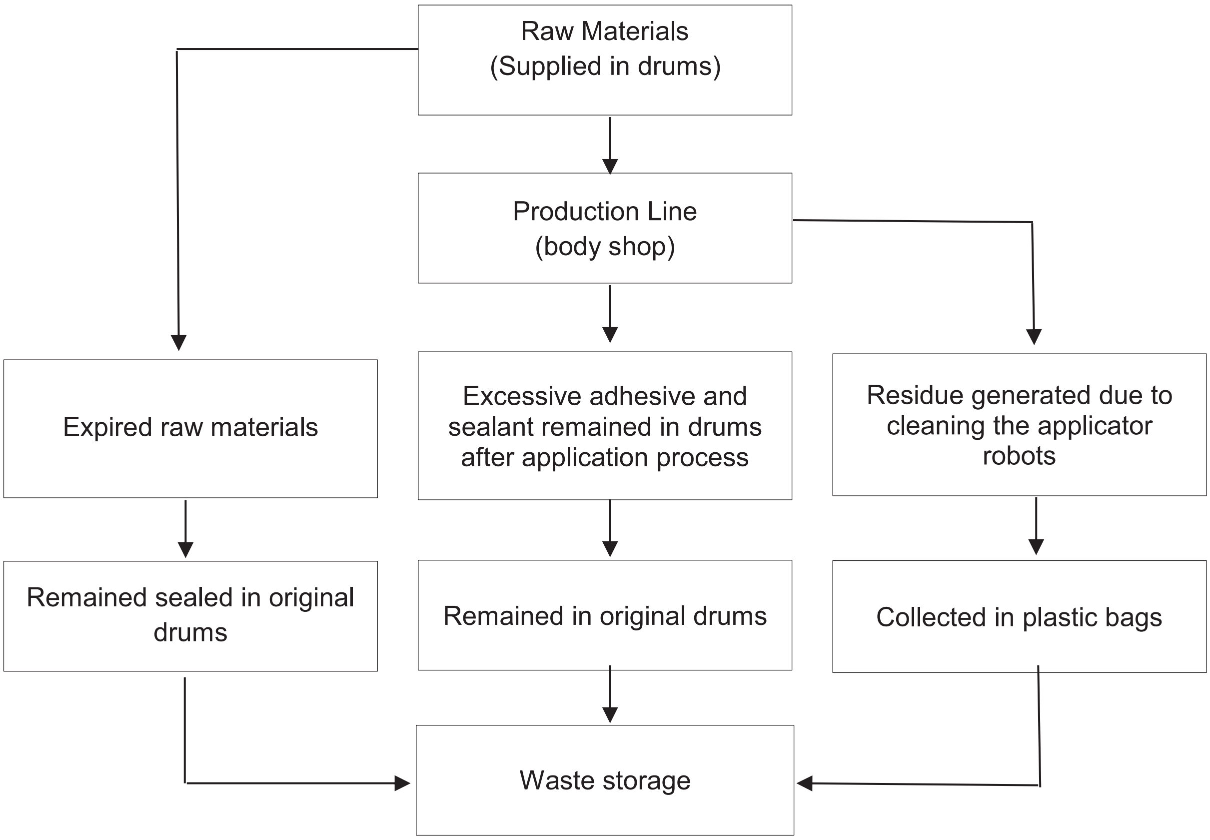
According to TABLE 5 and TABLE 6, the two products, Product A and Product B, are almost similar to technical and safety consideration point of view. It is pointed out that both products are hazardous for aquatic organisms, and they contain almost the same hazardous compounds. Therefore it remarks on the similarity in case of waste classification for the leftovers (residues) that are generated from these two products, as they both show the same hazard. Moreover, the technical similarity is a great point for further application of the residues from these two products. It indicates that it is possible to suggest the same destination that can make use of both residues as they would be similar. On the other hand, the researcher observation indicated that they both have a pasty structure, considering all the information together, it was decided to study their both residues as the main focus of the study.

4.2 CLASSIFICATION OF CHOSEN RESIDUE

4.2.1 Sources of Residue Generation

The studied adhesive and sealant materials which the “industry A” uses in the body shop section are supplied in the form of sealed drums containing uncured one-part formulation adhesive and sealant. The next step is to apply these adhesives and sealants on the target substrates and furthermore to cure the bond and finalize the process. The process of waste generation is illustrated in FIGURE 7.

FIGURE 7- FLOW CHART OF RESIDUE GENERATION PROCESS

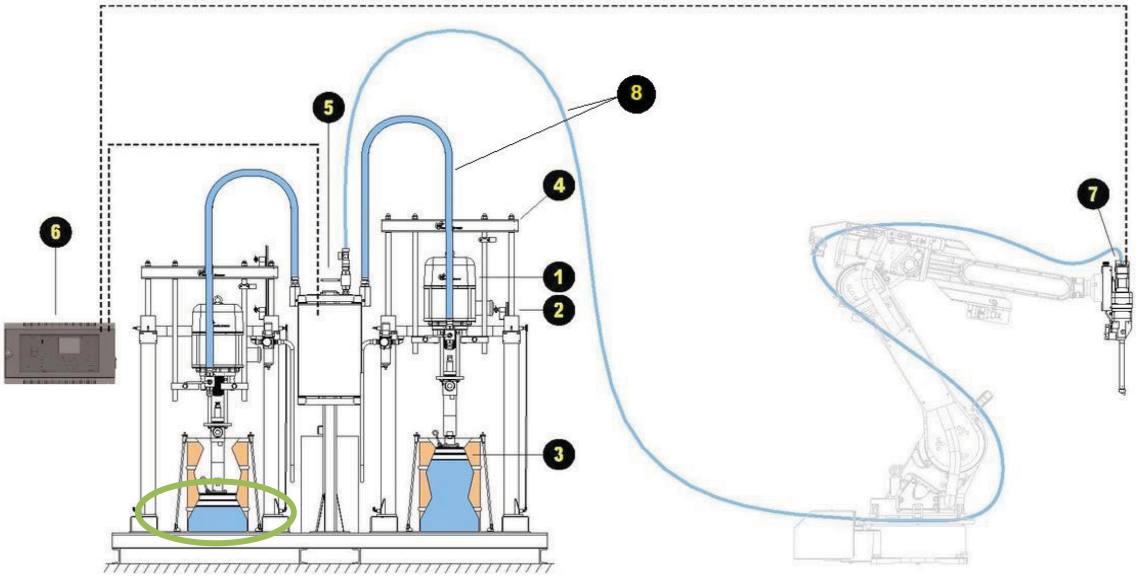


SOURCE: AUTHOR (2018).

As it is illustrated in FIGURE 7, the raw adhesive and sealant materials which are stored in the storage are meant to be used in production line, but due to insufficient storage plan, some of them are expired before being sent to the production line. Since it is not possible to use the expired materials due to the failure possibility in achieving the desired final bond quality, they will be considered waste (KINLOCH, 1990) and will be sent to waste storage station. On another hand, not all of these raw adhesive and sealant materials which are sent to the production line (body shop) will be used completely. The raw materials in the production line are applied on the target surfaces with the help of automated application systems (robots), and during the application process, some waste is generated. The main sources of adhesive and sealant waste in the production line are divided into two sections; the extra remained adhesive and sealant at the bottom of each drum and waste generated from the cleaning of the robots.

To have a better understanding of the application process and the applicator robots, FIGURE 8 provides a picture of the different parts of an adhesive and sealant applicator robot.

FIGURE 8- DIFFERENT PARTS OF APPLICATOR ROBOT



(1) Tandem piston pump. (2) End drum control (Inform about the end of the drum). (3) Follower plate. (4) Elevator. (5) Rexflow (Touch screen controller managing: Heated zone, Pump start & stop, Pressure regulation, Runaway protection). (6) B6 controller (Advanced flowrate controller). (7) Regulex (Electrical shotmeter, multi axis robotic compatible). (8) Heating hoses.

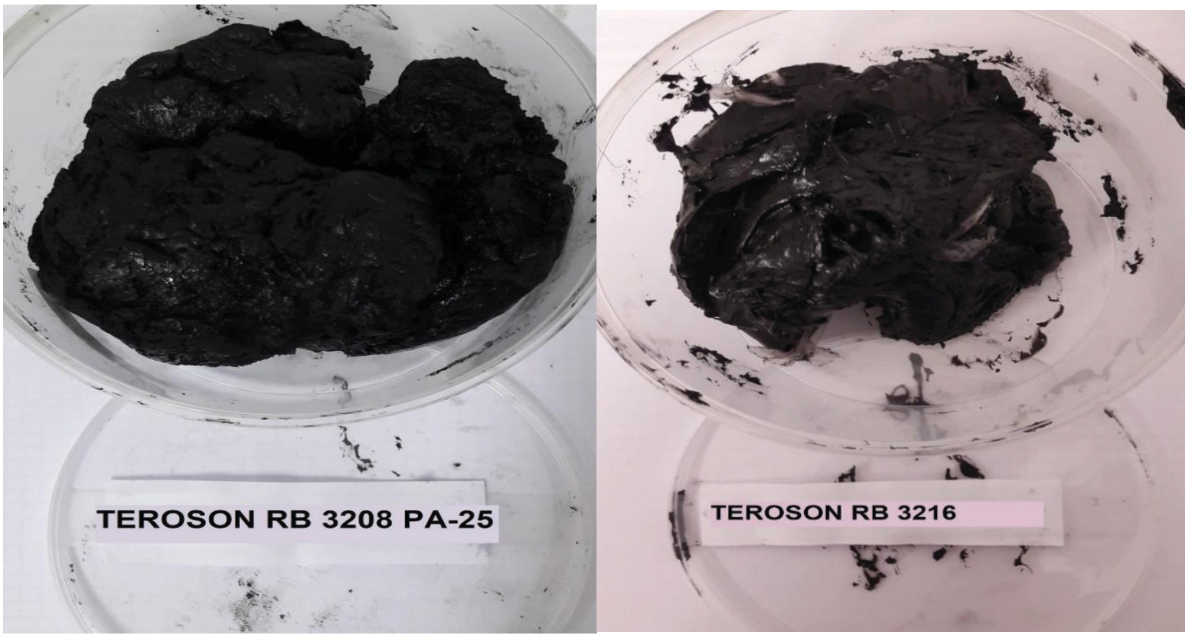
SOURCE: SAMES KREMLIN (2018).

As it is shown in FIGURE 8, the elevator (5) pushes the follower plate (3) down and when the follower plate arrived to the point of 90% distance from top of drum, it stops and 10% of raw material stay untouched at bottom of the drum (it is highlighted with a circle around the drum at FIGURE 8).

The three main processes of adhesive and sealant waste generation in the industry A is explained in detail below:

(1). approximately 90% of residue is generated after applying the uncured adhesive and sealant to the target substrates from the drums. Automobile producers apply the uncured adhesive and sealant with the help of an automatic application system (robot). The robot is connected to the adhesive and sealant drum and applies the material using a high-pressure pump. In order to cause no harm to the pump and to the robot, the process of application is designed in a way that approximately 10% of materials stay untouched at the bottom of each drum. These leftovers together with drums which contain them are sent to the residue’s station. to understand better how a leftover adhesive and sealant from application process looks like, following illustrates the residue samples of studied adhesive and sealants, Residue I and Residue II. FIGURE 9 shows the residues that are collected in the waste storage station of industry A to be send to laboratory for further physicochemical analysis.

FIGURE 9- STUDIED RESIDUES’ SAMPLES WHICH ARE GENERATED DURING APPLICATION PROCESS.



(Residue I) (Residu II)

SOURCE: AUTHOR (2018).

(2). The second part of the residues is generated during the process of cleaning the applicator robots. During the cleaning process, all the materials which are left in different parts of the applicator robot are pump out of the device and collected in plastic bags to be sent to the waste storage station. FIGURE 10 shows the residue that is generated during the cleaning process.

FIGURE 10- THE RESIDUE GENERATED DURING CLEANING PROCESS.

SOURCE: AUTHOR (2018).

(3). The third type of residues is the expired materials. It is not possible to use these materials for their designed application, so they are sent to the residue’s station as well.

During the presented study, the residues which are chosen for further studies are the leftovers from the application process which are sent to the waste storage station in their original drums. It is clear that no contamination will affect the residues according to this residue generation procedure. However due to exposure to ambient air and humidity, and changing in temperature during the residue storage period, the characteristics of uncured adhesive and sealant will change. According to KINLOCH (1990), polymerization and curing process in thermoset adhesives (Product A and Product B) happens in elevated temperatures, but it is possible that some chemical reactions even start at room temperature or out of specific storage environment. But this fact will not affect the residue in case of contamination. Therefore, it is clear that the residue is not contaminated by any external source of pollution.

As it mentioned in methodology, the addition of any hazardous contamination during generation process of a residue would have a direct effect on the classification of the mentioned residue, and the results in this study showed that no contamination affects the material during the generation process.

4.2.2 Classification

According to the norm, ABNT NBR 10004, solid wastes are classified into two groups of hazardous (class I) and non-hazardous (class II); and the latter group subdivided into non-inert (class II A) and the inert (class II B). A waste is classified as hazardous waste if its characteristics causes: a) Risk to public health, mortality, incidence of diseases or accentuating their rates; b) Risk to the environment when the waste is improperly managed, or shows any of toxicity, flammability, corrosivity, reactivity, or pathogenicity characteristics, or listed in the annexes A and B of the norm (ABNT NBR 10004, p.3, 2004).

The results of extra physicochemical tests which had been done by EP Analítica Laboratory does not show any violation to the limits presented in ABNT NBR 10004 in the case of flammability, corrosivity, and reactivity (ANNEX 2). Moreover, the pathogenicity factor is considered irrelevant to the studied residue. According to the results that EP Analítica Laboratory provided to the researcher the residues do not show any flammability, corrosivity, and reactivity nor fall into the categories of Annex A and B of ABNT NBR 10004 norm. Therefore the laboratory had been classified both residues as waste class II A (non-hazardous non-inert waste).

However, it is worth to mention that the SDS of both materials (original products) that the residues are generated from, shows that they are toxic to aquatic organisms and may cause long-term adverse effects in the aquatic system (ANNEX 1), and according to the norm ABNT NBR 10004 this toxicity is categorized as ecotoxicant. In the analyses that the EP Analítica Laboratory had been performed the information regarding the toxicity of the residues is neglected. Hence more information in this sector is needed to be sure if the residues contain no hazardous effect on the environment and could be classified as class II A.

Moreover, by reviewing the results of solubility and leaching tests (ANNEX 2), the presence of phenol in quantities over than the limits is evident. Phenol is a component that may result in nose, throat, eyes irritation, and skin burns in addition to acute toxic effects for species and aquatic ecosystems (SAHA et al., 1999). These results show the same hazard for the studied residue (Residue I and II), as it is mentioned in the SDS of both products which Residues I and II are generated from (TABLE 5 and 6).

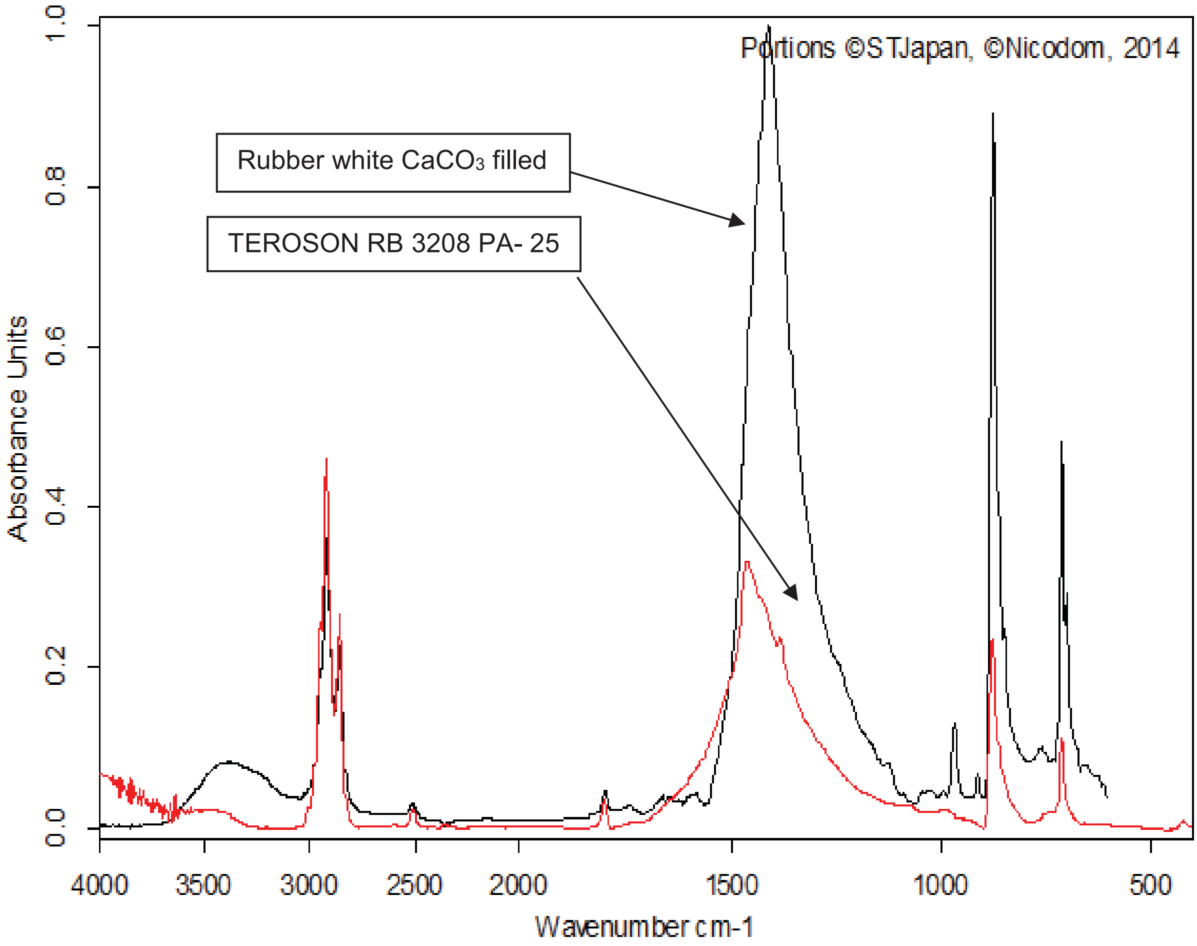
However, it is worth mentioning that predicted hazards are just existing as long as one adhesive or sealant stays in the uncured phase. As soon as the uncured adhesive and sealant materials are fully cured all the hazardous characteristics of them will fade (YANG et al., 2015). Therefore, suggesting a destination which provides the possibility for the uncured adhesive and sealant residues to be fully cured is a way to avoid any harmful effect to the environment and species.

4.3 RESIDUE'S POLYMERIC BASE IDENTIFICATION

The results of FTIR spectroscopy is presented in the form of a spectrum. The spectrum of the unknown residue is compared with the known materials' spectrum existing in the database of the © 2014 NICODOM software. The most similar spectrum to the unknown residue spectrum is chosen by the software. This known material indicate the major polymeric base existing in the residue. Since the two residues' sample were studied, the results are presented in two divided graphs.

The sample number (1) is a sample from Residue I. Comparing the results with the database of © 2014 NICODOM showed that the main polymeric base of residue is rubber white, and it is filled with $CaCO_3$. The results of the library search and its comparison with the FTIR spectrum of the sample can be found in ANNEX 3. The spectrum of sample number one and the most similar spectrum that is suggested by the software is illustrated in FIGURE 11.

FIGURE 11- FTIR SPECTRUM OF SAMPLE NUMBER (1) AND THE LIBRARY SEARCH RESULT.

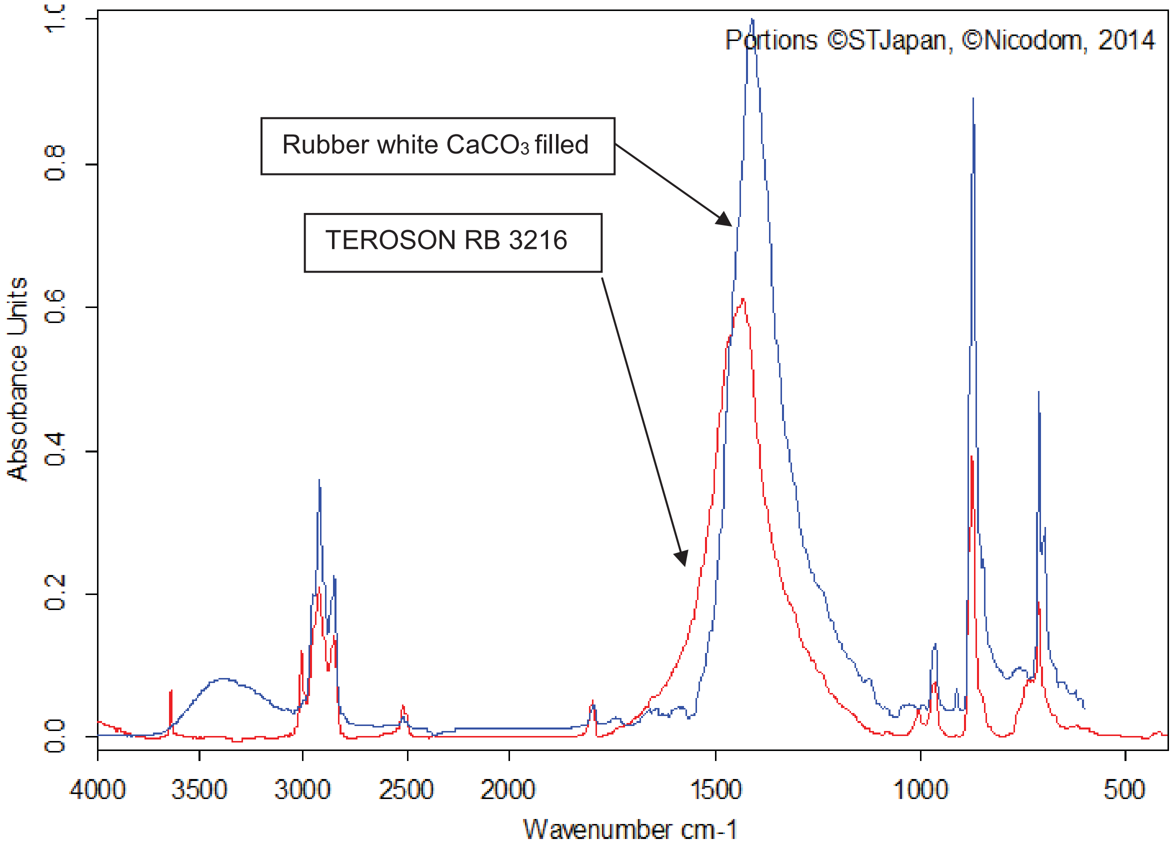


Black color line: rubber white $CaCO_3$ filled/ Red color line: TEROSON RB 3208 PA- 25 spectrum.

SOURCE: AUTHOR (2018).

The sample number (2) is a sample from Residue II. Comparing the results with the database of © 2014 NICODOM shows that the main polymeric base of residue is rubber white, and it is filled with $CaCO_3$. The results of the library search and its comparison with the FTIR spectrum of the sample can be found in ANNEX 3. The spectrum of sample number two and the most similar spectrum that is suggested by the software is illustrated in FIGURE 12.

FIGURE 12- FTIR SPECTRUM OF SAMPLE NUMBER (2) AND THE LIBRARY SEARCH RESULT.



Blue color line: rubber white $CaCO_3$ filled/ Red color line: TEROSON RB 3216 spectrum.

SOURCE: AUTHOR (2018).

By comparing the results of both residues' FTIR test, one can understand that both residues are similar. This result is additional proof, and a confirmation of the correctness of the decision had been made regarding choosing the two residues as the main focus of the study.

Furthermore, the results of the FTIR database search for both residues showed the rubber white (natural rubber) filled with $CaCO_3$ as the main polymeric base of the studied residues. Therefore, the suggested destinations should have the possibility of accepting materials with natural rubber as their main polymeric base.

Moreover, according to the TDS of the products which the studied residues are generated from, there are other ingredients existing in the formulation of the original adhesive and sealant. For instance, the existence of additives such as fillers, activator agents, blowing agents, etc. is an unavoidable part of an adhesive and sealant formulation. As it mentioned in the methodology, in general knowing the exact ingredients existing in one adhesive and sealant product is almost impossible. It is understandable by the fact that many producers try to keep their products' formulation secret. Therefore, identification of the main polymeric base of the studied residues and suggesting a reuse destination base on this information is the key factor in this study.

4.4 ALTERNATIVE USE OF RESIDUE

The results of the residues' polymeric base identification showed that both residues contain mainly rubber white (natural rubber) as the key constituent in their formulation. Moreover, knowing the residues' generation process, they did not undergo polymerization and curing process. This means that the studied residues do not fall into the category of cured rubber modified thermoset polymeric materials. Therefore, the available recycling methods which are recently used for thermosets would not be a suitable solution as the residues do not show the characteristic of a toughened rubber modified thermoset.

A short overview of the results of this study is provided in the following (In the next sub-sections details and supporting information regarding each result will be explained in advance):

In the first place, to answer the question "whether it is possible to reuse the studied residues in asphalt" technical and environmental safety aspects were reviewed. The results showed however it is technically possible to reuse the studied residues in asphalt (KANG et al., 2016; HASHEM et al., 2013; PAPAGIANNAKIS et al., 2012; RADHAKRISHNAN NAIR et al., 1998), but legally in developed countries such as Germany it is generally not allowed to distribute wastes in the environment without a legal basis or authorities' special permit. Moreover considering the environmental aspects, it is not recommended by the researcher to use the residues in the destinations which have direct contact with people or the environment.

In the next step, recovery of these materials in original adhesive and sealant products seem to be the best option. They can be used as a small portion of the feed for the preparation of new adhesives and sealants (TORMENTO, 2018).

Moreover, they can be used in small portions in any process that utilize rubber white, since it was the rubber white (NR) which was detected as the main polymer group exists in the residues, the suggestions which are offered in this study are based on the natural rubber’s applications.

4.4.1 Road Construction, Using the Residues in Asphalt

Reusing the studied residues in asphalt as an additive to asphalt binder was the idea that initiated this study. Therefore answering the question whether it is possible to use the uncured adhesive and sealant residues in asphalt or not is important. In order to answer this question, two aspects have been considered effective. The technical aspect and the environmental safety aspect.

In general, the possibilities of reuse and recycling have to be considered for all wastes, however only if the environment is not harmed by the practice (According to the German (and European) waste legislation (Kreislaufwirtschaftsgesetz (KrWG), EU waste directive (2008/98/EC) and Brazilian national solid waste policy, Law No. 12,305). In the latter sense it is generally not allowed to distribute organic or other harmful wastes in the environment (disguised landfilling - what cannot be landfilled, cannot be distributed in the environment). Every new waste a company wants to use as secondary material in construction must be tested on its equality to the original material (technical aspect) and its environmental safety.

Referring to the various researches had been done on using different polymeric materials including thermoset resins and rubbers as asphalt modifiers, and various tests which had been conducted on modified asphalts to assure that a better quality had been achieved by these modifications (KANG et al., 2016; HASHEM et al, 2013; PAPAGIANNAKIS et al, 2012; RADHAKRISHNAN NAIR et al., 1998), It can be concluded that technically it would be possible to use the target adhesive and sealant residues as an additive to asphalt formulation. At the moment most of the researches are investigating the effect of adding virgin polymeric materials as an additive to asphalt binder on the quality of asphalt, and there is no information on reusing the uncured polymeric materials residues. Therefore, it would be necessary to conduct further investigations and studies to assess the effect of the studied residues on the asphalt quality.

Regarding the environmental safety aspect, considering the results of leaching test, the reuse of the residues is not recommended. In the leachate from the uncured adhesive and sealant residues a violation to the limits in case of phenol is evident (ANNEX 2), and since during the asphalt preparation process there is no guarantee that the added residues become fully cured, an environmental risk regarding the reuse of these residues exist. Furthermore, in developed countries such as Germany, it is prohibited to distribute organic or other harmful wastes in the environment. Whatever cannot be landfilled, cannot be distributed in the environment as well. On landfill sites, the total organic content (TOC) is limited to 1 to 6% of mass depending on the landfill class (EEA, 2009; ETC/SCP, 2009). In the case of the residues which are studied in this work the TOC is much bigger than the maximum allowed limit. Moreover, in the relevant technical regulations for use of second-hand materials in asphalt the limits are even stricter, "Technische Lieferbedingungen (TL) für Asphalt im Straßenbau" and "TL für Bitumen im SB" are examples in which also the possible use of recycling materials is described. Therefore considering other developed countries point of view, reusing the studied residues in asphalt is not an accepted reuse destination as well.

4.4.2 Material recovery in the original compound

According to the SDS of Product A and Product B presented in ANNEX 1, the adhesive and sealant have rubber for modification, a large amount of CaO (desiccant), a vulcanization accelerator mercaptobenzothiazole disulfide (MBTS) in combination with sulfur as the cross-linker and zinc oxide (ZnO) as an activator. Additionally, a blowing agent and an expansion activator, the Phthalic anhydride is also presented in the formulation.

The leftovers could be easily recovered if there were not two factors interfering: the expansion of Azodicarbonamide and the Vulcanization by MBTS. However, it is proposed by TORMENTO (2018) to return the leftovers (residue) to the original compound in small quantities (10-30%). To return the materials to the original compound, it is possible to follow the next steps:

- Peptizing these leftovers in a cylinder mixer (maximum temperature 80°C).
- Using zinc stearate as the peptizing agent (start with 2-3 phr).
- Adding a retarder to avoid that the accelerator already in the beginning of decomposition continues to act.

- Adding 10-30% of leftovers in the original compound and analyze data.

Material Recovery in the original compound which is a conventional reuse option is considered to be one of the best options. However sending back the residue all the way back to its producer is not an economic solution (since the studied automobile industry use imported adhesive and sealant products), but interior adhesive and sealant manufacturers could have the possibility to use the residue in small portions for production of the same kind of new adhesive and sealants.

4.4.3 Material recovery in the products made of rubber

The results of FTIR spectroscopy showed that the rubber white (NR) is the main polymeric group exists in the residues. Additionally, the initial products that residues are generated from are thermoset adhesive and sealant. Therefore, it is expected that studied residues can be used in small portions as an additive to the products that have similar input components, and during their production process enough heat is applied in order to have the added residue cured.

In the first place, In order to have a better understanding of the ingredients present in the residues, TABLE 7 is provided below.

TABLE 7- INGREDIENTS WITHIN THE RESIDUE I AND II.

Component	**Residue II**	**Residue I**	**Information**	**Source**
	Percentage			
Limestone	------	30-60	Filler	SDS, Annex 1
Calcium carbonate	40-50	10-30		SDS, Annex 1
Calcium oxide	1-5	1-5	Desiccant	SDS, Annex 1
Distillates (petroleum), solvent- refined light paraffinic	1-5	10-30	-	SDS, Annex 1
Carbon black	0.1-1	1-5	Filler	SDS, Annex 1
Zinc oxide	1-5	0.1-1	Activator agent	SDS, Annex 1
Phthalic anhydride	------	0.1-1	blowing agent	SDS, Annex 1
Di(benzothiazol-2-yl) disulphide	1-5	------	Vulcanization accelerator	SDS, Annex 1
Sulfur	1-5	------	Vulcanizing agent	SDS, Annex 1
Phenol-formaldehyde polymer	1-5	------	-	SDS, Annex 1
Methenamine	0.1-1	------	-	SDS, Annex 1
Rubber white (NR)	The main polymeric base of both residues (qualitative information)			FTIR Spectroscopy, Annex 3

SOURCE: AUTHOR (2018).

The information about the ingredients which are presented in TABLE 7 is adapted from the SDS of the products which the studied residues are generated from except the info regarding the polymeric base of the residues. It is worth to mention that all of the ingredients which are existing in the original products will be existing in the uncured adhesive and sealant residues as well, and that is why the information provided by the products' producer (in SDS) is valuable information and help to know more about the residues' ingredients. TABLE 7 indicates the fact that there are many components within the residues. As it mentioned in section 3.3 knowing the exact components of the residues and the amount of them is almost impossible. Therefore, choosing one main ingredient to continue the study base on it was important. However, it is just a point to start the further investigations. Another effective factor that defines whether or not it is possible to reuse the residue in the suggested destination is the compatibility of the residue with the other input materials of one proposed destination. This sentence points out the effect of the residue as a whole with all different components it consists on the final product quality, not just base on one main polymeric ingredient; and the approbation of this fact needs additional studies which are beyond the scope of this work.

The other factor that needed to be considered for suggesting a reuse destination is the environmental safety aspects. Knowing the manufacturing process of the products in the final destinations is one of the indicators that can help to decide whether it is possible to make use of the studied residue in small portions during the manufacturing process or not. Therefore among products which contain the natural rubber (similarity between the input materials of suggested destination with the main polymeric base of residues) the ones which present less risk for human health and the environment and have a curing step during their manufacturing process were chosen. Following are the suggested products:

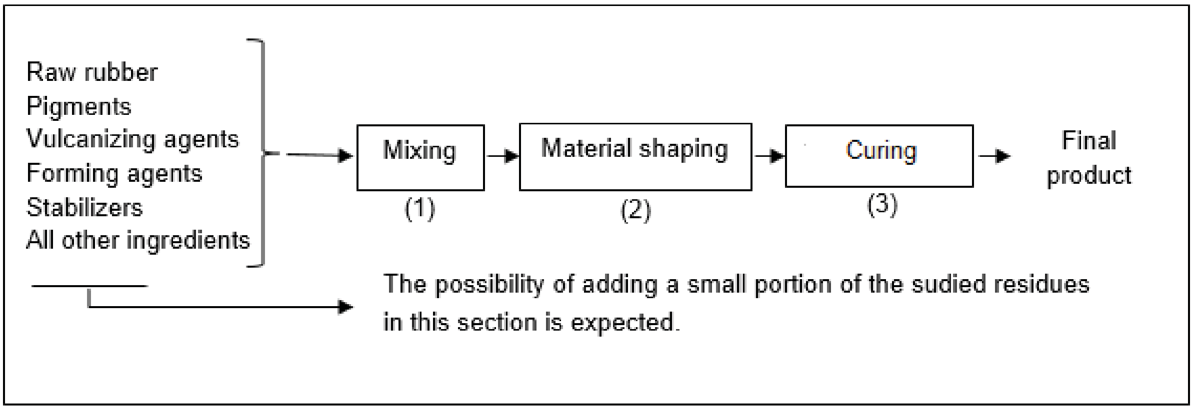
1. Tires, both pneumatic tires (cars, bicycles, motorcycles, buses, trucks, and heavy equipment) and solid tires (casters, carts, lawnmowers, and wheelbarrows). However, this study recommends reuse of the studied residues in a less critical application such as solid tires. Pneumatic tires are high-quality products which need to undergo several tests to ensure the safety of users and the high quality of the product in the final section of their production. Furthermore, it is less probable that a pneumatic tire manufacturer willing to risk

the quality of his product by using a second-hand material in the process, though from the technical and environmental safety point of view it would be a possible option.

2. Industrial products such as conveyor belts, transmission and elevator belts, industrial lining, hoses and tubes, and other applications of natural rubber such as gaskets for door and window profiles, matting, flooring, and dampeners are among the potential destinations that are suggested in this study for reuse of the studied residues. However, as it explained in the literature of this study there are various applications for natural rubber such as sporting goods, clothing, toys, etc. which this study does not suggest them, since using a second-hand industrial material like the studied residues cause a direct contact of these materials with people and it may pose a risk to the human health.
3. Polymer matrix composite manufacturing is another section which can benefit from these residues. There are various kinds of polymer matrix composites. Literature indicated that various thermoset materials had been used depending on which characteristics are desired for the final polymer matrix composite product (HOA, 2018; MIDDLETON, 2016; WANG et al. 2011). Moreover, many studies show the possibility of using natural rubber in composite manufacturing (FLINK et al., 1990; SUI et al., 2008; MENTE et al., 2016; JACOB JOHN et al., 2008; NAIR et al., 2014).

FIGURE 13 summarizes the information was gathered in the literature section of this study regarding the manufacturing process of suggested destinations and points out in which part of these mentioned products’ manufacturing process one can add the studied residues. The literature showed that the manufacturing process in all of these products is similar (KURIAN et al., 2011; PEARSON, 1906; BANDARA, 2011; BC, 2018; KRP, 2018; CROWTHER, 1998; NWB, 2018; BRAVO et al., 2017; SME, 2018). FIGURE 13 is illustrating the main three steps that happen during the production of all of the suggested rubber goods.

FIGURE 13- GENERAL VIEW OF SUGGESTED RUBBER GOODS PRODUCTION



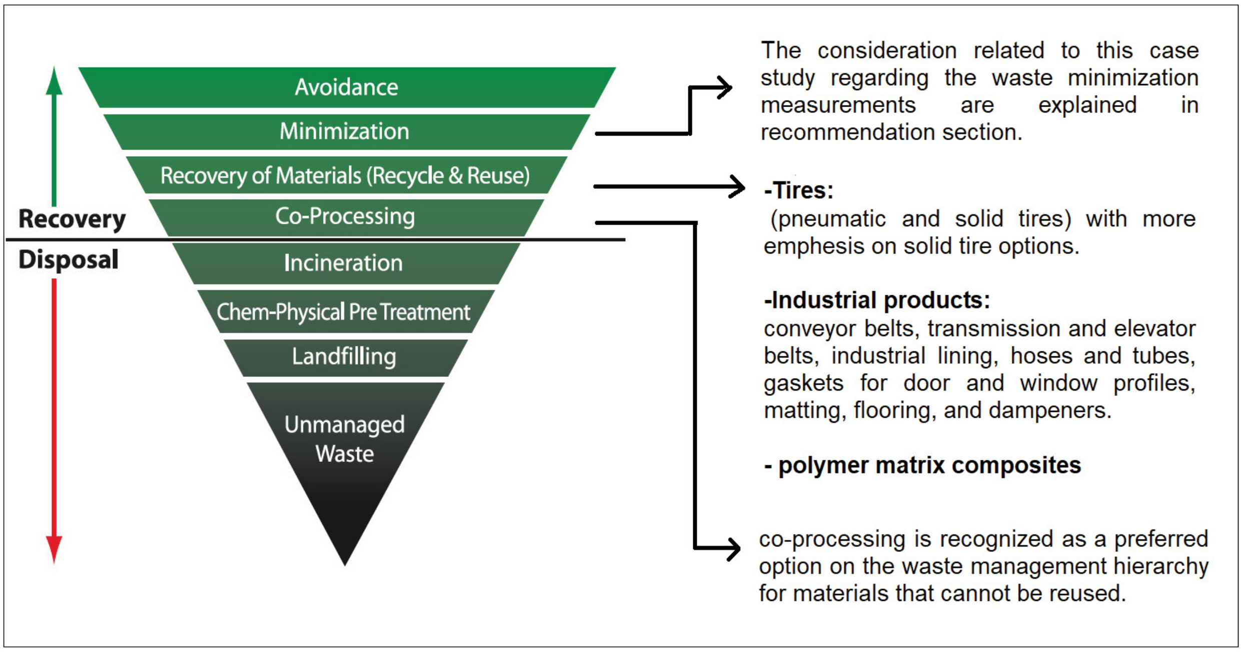
SOURCE: AUTHOR (2018).

As it is shown in Figure 13, the first step is mixing the raw rubber with pigments, vulcanizing agents, foaming agents, stabilizers, and all other special ingredients. Internal mixers, kneaders, mixing mills, or extruders are among the devices which have been used for mixing. Next step is to form the mixed rubber compounding into the desired shape; this section depending on the product (i.e., pneumatic tires) can be more complicated and needs additional steps such as material processing. Usually, this step is the step which can vary depending on one product to another. For instance, the compounded rubber is passed through a die with the desired pattern under pressure of an extruder in case of rubber gasket manufacturing for window or door profiles (CROWTHER, 1998), or it is molded under pressure and heat in case of tire manufacturing (ISHIKAWA, 2011). The final step is the curing step and can happen using a variety of processes including cooking ovens, microwaves, and hot air or water heating, and they can be part of a continuous or batch process.

According to the suggested rubber goods production processes (FIGURE 13), it seems that the uncured rubber modified thermoset adhesive and sealant residues could be reused inform of additive in small quantities to the raw materials. The reason behind this statement is the similarity between the ingredients present in the residues and the raw materials have been used for rubber goods production. The only component in the residues that may cause difficulties for reusing is high quantities of limestone and calcium carbonate fillers (TABLE 7). These materials typically are not existing in the proposed rubber goods formulation. On the other hand, in these processes, the uncured residues would undergo the curing process. Therefore, they no longer cause any health or environmental risks. According to the results were achieved in waste classification section, the studied residues contain phenol in quantities over than the limits. Moreover, the chemically reactive monomers/oligomers, hardeners and crosslinking agents determine the potential health and environment hazards of these uncured residues. However, during the curing process, all of these hazardous compounds would be locked in the long-change polymerized molecules. Therefore, once the uncured residues are fully cured, there will be no longer any hazard for environment or health (YANG et al., 2015).

Since the study started with the goal to follow the waste hierarchy concepts, the suggested destinations, are presented in FIGURE 14 based on waste hierarchy.

FIGURE 14- RESIDUES MANAGEMENT OPTIONS BASED ON WASTE HIERARCHY.



The consideration related to this case study regarding the waste minimization measurements are explained in recommendation section.

-Tires:
(pneumatic and solid tires) with more emphesis on solid tire options.

-Industrial products:
conveyor belts, transmission and elevator belts, industrial lining, hoses and tubes, gaskets for door and window profiles, matting, flooring, and dampeners.

- polymer matrix composites

co-processing is recognized as a preferred option on the waste management hierarchy for materials that cannot be reused.

SOURCE: THE AUTHOR (2018).

As it is demonstrated in FIGURE 14, according to the waste hierarchy, concepts such as minimization and material recovery have a greater position in compare to the co-processing which is an energy recovery option. some recommendations were provided for the studied industry (industry A) regarding the minimization measurements. The measurements are explained in detail in the following section. Moreover, as the studied uncured adhesive and sealant residues are not polymerized yet, a vast range of options for reusing them is available. The study recommended the reuse of the uncured adhesive and sealant residues for production of tires (both pneumatic and solid tires), Industrial products such as conveyor belts, transmission and elevator belts, industrial lining, hoses and tubes, gaskets for door and window profiles, matting, flooring, dampeners, and polymer matrix composites.

5 RECOMMENDATION AND CONCLUSION

5.1 RECOMMENDATIONS

There would be a couple of recommendations offered in this study, following presents the recommendations regarding the process of adhesive and sealant's residues management in the studied automobile industry:

The most important way to reduce waste is to generate less in the first place, so reducing the waste generation staying in the first place. Reuse is another option for waste prevention which seizes the opportunity of using the material for its original purpose (conventional reuse), or to fulfill a different function (creative reuse or repurposing). Waste prevention offers the greatest environmental benefits and costs savings. Following is the consideration that is proposed for waste prevention.

I. Reduce

In the first place by having an appropriate raw material storage plan that is controlled in a way that the oldest stock is used first, one can reduce the amount of expired adhesives and sealants that have no longer possibility of being used in their designed application and normally end up as waste.

The next step is minimizing the amount of generated residues in the application process. Here, there are some recommendations for (1). Engineers who design the production line in automobile industry, (2). The manufacturers who produce the automated adhesive and sealant applier robots. Each of the mentioned societies can play a significant role in adhesive and sealant waste reduction in the automobile industry.

In the first place, if an engineer who designs the production line in an automobile industry chooses the right automated application device with the capacity that matches the production line requirements, no excessive adhesive and sealant residue would be expected. As an instance, in the presented study it is observed that the automated applier which applies the SIKAPOWER 492, only works with big drums of raw materials. However, the consumption is a small portion, and small drums of materials are enough to meet the production line's needs.

On the other hand, the existence of automated applicator devices that are equipped with a pump that let the industry use the raw material in the maximum level until the material is finished completely in each drum is missing. The automated industries need devices which can guarantee the 100% usage of raw materials. For example at the moment in the studied automobile industry to cause no harms to the pump and the applicator robot, about 10% of raw material at the bottom of each drum stay untouched.

II. Reuse

During this study, the main focus was on finding the reuse options. As the studied residues are non-polymerized materials, they have a high potential to be used in various applications as second-hand input materials. In all suggested destinations in this study, two factors were considered important: 1. the existence of a similarity between the raw input materials of the chosen destination and the significant ingredients within the studied residues, and 2. the existence of the possibility for the residues to become fully cured after being reused in the suggested destination. However, it should be mentioned that if one destination meets these two criteria does not mean that the residues will be accepted by the destination for reuse. Another effective factor that defines whether or not it is possible to reuse the residue in the suggested destination is the compatibility of the residue with other input materials, and the approbation of this fact in each suggested destination needs further studies.

III. Co-processing

The fact that co-processing is a “recovery” process indicates its importance as an environmentally friendly option. Therefore, after prevention, reduce, reuse and recycle it is the next valuable waste management act. Since proving the possibility of reusing a waste in one destination could be a complicated and long process, this study still recommends the co-processing option as an environmentally sound solution to the studied residues.

5.2 CONCLUSIONS

At the moment there is no information or study on the alternative use of residues generated from adhesives and sealants application processes. If the users utilize the raw materials in the right way with the right-designed application machines, no residue from the application processes will be generated, however in reality, the studied automobile industry (industry A) is facing residues that are more or less equal to 10% of whole raw materials consumption. Therefore, it is important to pay more attention to this issue and try to bring these potential materials back into their life cycle.

It was the first phase in this study to gather all the information regarding the studied residues to define the residues' classification, characteristics and properties. The results of the study showed that the chosen residues which were generated from rubber based thermoset adhesives and sealants have rubber white filled with $CaCO_3$ as their main ingredient. According to the information provided by EP Analítica Laboratory on the waste classification, the residues were classified by the mentioned laboratory as non-hazardous non-inert waste (class II A) according to the Brazilian norm ABNT NBR 10004. However, the results of solubility and leaching tests showed the presence of components that pose health and environmental risks such as phenol in quantities over than the limits.

To have the uncured adhesive and sealant residues reused in the suggested destination without causing any health or environmental risk, the applications that have a curing step in the manufacturing process of them were chosen, and this was because fully cured adhesive and sealants are considered as non-toxic and safe materials. Therefore, among the polymeric product manufacturing processes, the ones that can use rubber white in their production process and have curing step during the manufacturing were selected.

Since the studied uncured adhesive and sealant residues are not polymerized yet, a vast range of options for reusing them is available. The study recommended the reuse of the uncured adhesive and sealant residues for production of tires (both pneumatic and solid tires), Industrial products such as conveyor belts, transmission and elevator belts, industrial lining, hoses and tubes, gaskets for door and window profiles, matting, flooring, dampeners, and polymer matrix composites.

It is not recommended in this study to reuse the residues in the applications that bring the material in direct contact with people or the environment. For instance, applications such as asphalt, or rubber consumer goods like clothing, toys, etc. are not recommended. This is due to the fact that even low risks to human health or environmental safety are not desired.

This study recognizes the possibility of using the studied residues in any industry which uses rubber white in its production process and provides an opportunity for the uncured adhesive and sealant residues to become fully cured during the process. But, the effect of using a second-hand material in all these various options needs to be studied in particular, and the compatibility of the residues with other polymeric compounds existing in each process needs to be investigated.

REFERENCE

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – ABNT: NBR 10004 - Resíduos sólidos – Classificação (Solid waste – Classification). Rio deJaneiro. Segunda edição: 31.05.2004. 77p.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – ABNT: NBR 10007 – Amostragem de resíduos sólidos (Sampling of solid residues). Rio deJaneiro: Segunda edição 31.05.2004. 25p.

BANDARA SA.; **1.2 Tire manufacturing process**. 2011. Available at: <http://dl.lib.mrt.ac.lk/bitstream/handle/123/1881/93951%20Chap%201.pdf?sequence=3>. Accessed on: July 2018.

BEX, G.; SEVENO, D.; DE KEYZER, J.; DESPLENTERE, F.; VAN BAEL, V. Wetting measurements as a tool to predict the thermoplastic/thermoset rubber compatibility in two-component injection molding. DOI: 10.1002/app.46046. J. Applied Polymer Science. 135. 46046. 2018.

Blog of Bulldog Castors Ltd (BC). Rubber polymers for caster wheels. Available at: <http://www.bulldogcastors.co.uk/blog/rubber-casters/>. Accessed on: July 2018.

Blog of P Strouth LLC- Industrial Material Handling Equipment (**IMHE**). © 2018 at Homestead™. Available at: <http://www.pstrouth.com/Casters.html>. Accessed on: July 2018.

BRAVO, A.; VIEIRA, D. **Chapter 21: Design and Manufacturing of Sustainable Composites.** Handbook of Composites from Renewable Materials. © 2017 Scrivener Publishing LLC. 14 July 2017

BRENTIN R.; SARNACKE PH. **Rubber compounds: a market opportunity study**. Omni tech international, Ltd. September 2011.

CHARLES E.; CARRAHER Jr. **Chapter 10: Rubbers (Elastomers).** Giant Molecules: Essential Materials for Everyday Living and Problem Solving, Second Edition. Copyright © 2003 John Wiley & Sons, Inc. DOI: 10.1002/0471457191. August 2003.

CROWTHER B.G. **Rubber Extrusion: Theory and Development**. ISmithers Rapra Publishing. Polymers - 102 pages. 1998.

EEA, 2009: ‘**Diverting waste from landfill**: effectiveness of waste management policies in the European Union’. EEA Report No 7/2009. Available at: <http://www.eea.europa.eu/publications/diverting-waste-from-landfill-effectiveness-of-waste-management-policies-in-the-european-union>.

ETC/SCP, 2009: The ETC/SCP “**Country fact sheets on waste policies** – 2009 edition”, Available at: <http://scp.eionet.europa.eu/facts/factsheets_waste/2009_edition/factsheet?country=DE>.

ENGELS, T. Thermosets (Second Edition) Structure, Properties, and Applications. **Chapter 10: Thermoset adhesives**. Elsevier. 2018. Pages 341–368.

EUROPEAN COMMISSION. Waste Framework Directive (2008/98/EC). Archived from <http://ec.europa.eu/environment/waste/legislation/a.htm> on May 08, 2018.

EVANS, A.; EVANS, R. Creating markets for recycled resources, **The Composition of a Tyre: Typical Components**. Project code: TYR0009-02. 27 February 2006. Published by: The Waste & Resources Action Programme. The Old Academy, 21 Horse Fair, Banbury, Oxon OX16 0AH

FLINK P.**;** STENBERG B. **Mechanical properties of natural rubber/grafted cellulose fiber composites. Polymer international**. Volume22, Issue2. Pages 147-153. 1990.

GOTRO, J.; PRIME, R.B. **Thermosets**. 15 February 2017. Encyclopedia of Polymer Science and Technology. Online ISBN: 9780471440260. John Wiley & Sons. Available at: <https://doi.org/10.1002/0471440264.pst519.pub2>.

HASHEM M. D.; RASHWAN N. K.; **The influence of resin modifiers on the performance of hot mix asphalt**. Journal of Engineering Sciences, Assiut University, Faculty of Engineering, Vol. 41, No. 3, May. pp. 867-885. 2013.

HERMANN O., RAINER W., GUNTHER D.; **Adhesives, 1. General.** Ullmann's Encyclopedia of Industrial Chemistry. John Wiley and Sons publisher. January 2010.

HERMANN O.; RAINER W.; GUNTHER D.; **Adhesives, 2. Applications**. Ullmann's Encyclopedia of Industrial Chemistry. John Wiley and Sons publisher. January 2010.

HOA S.V.; **2.1 Manufacturing of Composites – An Overview.** Comprehensive Composite Materials II. Volume 2. Pages 1-23. Elsevier. 2018.

ISHIKAWA Y. **Systematic Review of Tyre Technology.** National Museum of Nature and Science Vol.16, 2011.

JACOB JOHN M.; VARUGHESE K. T.; THOMAS S.; **Green Composites from Natural Fibers and Natural Rubber: Effect of Fiber Ratio on Mechanical and Swelling Characteristics.** Journal of Natural Fibers. Volume 5- Issue 1. Pages 47-60. 2008.

KANG Y.; WU Q.; JIN R.; YU P.; CHENG J. **Rubber-like Quasi-thermosetting Polyetheramine-cured Epoxy Asphalt Composites Capable of Being Opened to Traffic Immediately.** Scientific Reports volume 6, Article number: 18882. 2016.

KHAN, I.; POH, B.T. **Natural Rubber-Based Pressure-Sensitive Adhesives: A Review**. Journal of Polymers and the Environment. 2011. Volume 19, Number 3, Page 793.

KIM N. H.; KIM H. S. **Toughening Method and Mechanisms for Thermosets**. DOI 10.1002/app.22334. Published online in Wiley InterScience. J. Applied Polymeric Science 98: 1663–1667, 2005.

KINLOCH, A. J. **Adhesion and Adhesives Science and Technology.** Department of Mechanical Engineering, Imperial College of Science and Technology, University of London. Kluwer the language of science. Cambridge University Press. Reprinted 1990.

Kismet Rubber Products (**KRP**) - **Extruded Rubber Materials**. Available at: <https://www.kismetrubberproducts.com/materials.html>. Accessed on: July 2018.

KLOSOWSKI, J.M., Lueder, T.B., and Vandereecken, P. **Sealants**, Kirk Othmer Encyclopedia of Chemical Technology, 5th edn, John Wiley & Sons, Hoboken, NJ, online DOI: 10.1002/0471238961. 2017.

KURIAN T.; MATHEW N. M. **Chapter 4: Natural Rubber: Production, Properties and Applications.** Biopolymers: Biomedical and Environmental Applications, Susheel Kalia, Luc Avérous. Copyright © 2011 Scrivener Publishing LLC. DOI: 10.1002/9781118164792. 27 September 2011.

MARTÍNEZ, J. M. M.; **Chapter 13 – Rubber base adhesives.** Adhesion Science and Engineering (2002), Pages 573–675. Volume 2. **Elsevier.** Available online: 2 September 2007.

MENTE P.; MOTAUNG TE.; HLANGOTHI SP. **Natural Rubber and Reclaimed RubberComposites – A Systematic Review.** iMedPub Journals. Polymer Sciences ISSN 2471-9935. Vol. 2 No. 1: 7. 2016.

MERZ Peter W., **BURCHARDT** Bernd, **JOVANOVIC** Dobrivoje. Chapter 10, **Adhesive Bonding – A Universal Joining Technology**, Automotive Paints and Coatings, Second Edition, P. 367-375, May 2008.

MIDDLETON B.; **3 - Composites: Manufacture and Application.** Design and Manufacture of Plastic Components for Multifunctionality Structural Composites. Pages 53-101. Elsevier. 2016.

MORTON M. Elastomers, Synthetic, Survey. Kirk-Othmer Encyclopedia of Chemical Technology. 18 September 2009.

NAIR A.B.; JOSEPH R.; **9 - Eco-friendly bio-composites using natural rubber (NR) matrices and natural fiber reinforcements.** Chemistry, Manufacture and Applications of Natural Rubber. Pages 249-283. 2014.

Next What Business (**NWB**) - **Rubber floor mats making small-scale manufacturing**. Copyright © 2018 NextWhatBusiness. Available at: <https://nextwhatbusiness.com/rubber-floor-mats-making-small-scale/>. Accessed on: July 2018.

Niir Project Consultancy Services (NPCS) Board of Consultants & Engineers. The Complete Technology Book on Industrial Adhesives. ASIA PACIFIC BUSINESS PRESS Inc., Oct 1, 2008 - Adhesives - 592 pages.

PACKHAM D.E. Eco-efficient Construction and Building Materials. Chapter 15, **the environmental impact of adhesives**. Elsevier. 2014. Available at: <https://doi.org/10.1533/9780857097729.2.338>.

PAPAGIANNAKIS A. T., MASAD E. A. **Pavement Design and Materials**. Chapter 5, Asphalt Materials. Pages 107-160. June 2012.

PEARSON H.C. Rubber tires and all about them: pneumatic, solid, cushion, combination, for automobiles, omnibuses, cycles, and vehicles of every description. The India rubber publishing company. New York. 1906.

PETRIE, E. M. **Handbook of Adhesives and Sealants.** 2nd Edition. McGraw Hill Professional, Jan 2, 2007.

PIELICHOWSKI J.; NJUGUNA J. **Chapter 7: Elastomers.** Dirk Lehmhus; Matthias Busse; Axel S. Herrmann; Kambiz Kayvantash. Structural Materials and Processes in Transportation. DOI: 10.1002/9783527649846. Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA. 12 April 2013.

QIN H.; KIM G.-M.; FANG X.; SUN F. C.; MATHER P. T. **Hybrid Epoxy-Based Thermosets Based on Polyhedral Oligosilsesquioxane: Cure Behavior and Toughening Mechanisms.** 1 June 2003. © 2003 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 3299 –3313, 2003.

RADHAKRISHNAN NAIR N.; N. M. Mathew; Sabu Thomas; Prabha Chatterjee; M. A. Siddiqui; **Physical and rheological characteristics of liquid natural rubber modified bitumen**; First published: 07 December 1998.

REVALORE- Revalore Coprocessamento e Engenharia do Meio Ambiente. available at: <http://www.revalore.com.br/site/>. Accessed: July 2018.

RIGHTTURN. Tire-guide, subsection: Solid tires. Copyright 2018 Dealer Tire, LLC. Available at: <https://www.rightturn.com/tire-guide/solid-tires/>. Accessed on: July 2018.

SAHA N. C.; BHUNIA F.; KAVIRAJ A.; **Toxicity of Phenol to Fish and Aquatic Ecosystems.** Bulletin of Environmental Contamination and Toxicology. Volume 63. Issue 2. pp 195–202. August 1999.

SAMES KREMLIN- powertrain gasketing solution. Available at: <https://www.sames-kremlin.com/usa/en/solutions-powertrain-gasketing-solution.html>. Accessed by the author on June 2018.

SILVA NETO, J. B. Informação da Volkswagen do Brasil Indústria de Veículos Automotores. São Jose dos Pinhais – PR. 26. Jan. 2018. Verbal information.

SIMTEC. Thermoplastics and Thermosetting Plastics: Why They Work Together. February 16, 2016. Available at: <https://www.simtec-silicone.com/thermoplastics-and-thermosetting-plastics-why-they-work-together/>. Accessed on: 3/06/2018.

SKEIST, I. **Handbook of Adhesives.** 3rd Ed., Chapman & Hali publisher. New York, NY. 1990.

SME- Fundamental Manufacturing Processes Study Guide, DV02PUB2. © 2018 SME. Available at: <www.sme.org/WorkArea/DownloadAsset.aspx?id=73718>. Accessed on: July 2018.

SPROVIERI, J. Adhesives and Automobiles. ASSEMBLY magazine. December 17, 2007. Website link: <https://www.assemblymag.com/articles/85099-adhesives-and-automobiles>. Accessed on: 3/18/2018.

SUBRAMANIAN, M. N. **Introduction to Polymer Compounding: Raw Materials, Volume 1**. Smithers Rapra Technology Ltd. Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK. 2014.

SUI G.; ZHONG W. H.; YANG X. P.; YU Y. H.; ZHAO S. H. **Preparation and properties of natural rubber composites reinforced with pretreated carbon nanotubes**. Polymers for advanced technologies. Volume19, Issue11. Pages 1543-1549. November 2008.

TISSOT, M. REVALORE- Coprocessamento e Eng. do Meio Ambiente. Curitiba – PR. 10.novembro.2017. Verbal Information.

TORMENTO, L. Rubber-based adhesives [personal message]. Message received from: <luistormento@ltquimicos.com.br>. 14/03/2018.

VOLKSWAGEN- Imprensa Volkswagen, Fábrica da Volkswagen do Brasil no Paraná reduz em 80% a destinação de resíduos para aterro industrial, 22 de junho de 2016. Available at: <http://vwbr.com.br/ImprensaVW/Release.aspx?id=f2ba281e-fd41-4fa5-a633-a6ae98b0375d>. Accessed: July 2018.

VOLKSWAGEN- Imprensa Volkswagen, Home, Factories, São José dos Pinhais (PR). Available at: <http://vwbr.com.br/ImprensaVW/page/Sao-Jose-dos-Pinhais-(PR).aspx>. Accessed: July 2018.

WANG R.M.; ZHENG S.R.; ZHENG Y.P. **Polymer Matrix Composites and Technology.** Woodhead Pub. Technology & Engineering - 555 pages. 2011.

YANG, M.; Rosentrater K. A.; **Environmental effects and economic analysis of adhesives: a review of life cycle assessment (LCA) and techno-economic analysis (TEA).** Agricultural and Biosystems Engineering Conference Proceedings and Presentations*.* 437. Available at: <https://lib.dr.iastate.edu/abe_eng_conf/437>. 2015.

ANNEX 1

TECHNICAL AND SAFETY DATA SHEET OF PRODUCTS WHICH CHOSEN RESIDUES ARE GENERATED FROM

TEROSON

Technical Data Sheet

TEROSON RB 3216

December 2013

PRODUCT DESCRIPTION

Technology	Rubber
Product Type	Antiflutter Adhesive

TEROSON RB 3216 is a heat curing, solvent free, one component adhesive, based on Rubbers. The high viscosity of the product leads to an excellent sag resistance and makes it wash-off resistant without pregelling or precuring against aqueous cleaning and pretreatment agents. TEROSON RB 3216 adheres well to oily steel sheets, aluminum and zinc coated surfaces. The material is flexible and little dependent of changes in temperature. TEROSON RB 3216 chemically cross-links at temperatures above 140 °C. Due to the good compatibility to E-coat paint it offers a safe corrosion protection, even at boundary areas. TEROSON RB 3216 can be painted after curing.

APPLICATION AREAS

TEROSON RB 3216 is used as antiflutter in the automotive body shop and shows good adhesion on oily surfaces. It is specially designed as stiff antiflutter material to bond parts like engine hoods or trunk lids. It is recommended for use, when wash-off resistance must be obtained without pre-gelling or pre-curing, and where a high degree of elasticity is required over a wide temperature range.

TECHNICAL DATA
(Typical Test Results)

Uncured	
Colour	black
Density	approx. 1.5 g/cm³
Consistency	pasty
Solids	> 98 %
Viscosity (DIN 54458)	300 Pa.s
Equipment	P/P 25 mm
Frequency	10 Hz
Deformation	10 %
Temperature	45 °C
Sag resistance	
10 min at 23 °C	no sagging
30 min at 180 °C	no sagging
Cured (25 min. at 175 °C)	
Expansion rate	approx. 10 %
Shear strength (DIN EN 1465)	> 1.4 MPa
bonding area	25 x 20 mm
layer thickness	2 mm
substrate	HDG / EGS 0.75 mm
Shore A hardness (DIN 53505)	approx. 60
Temperature resistance	
short exposure (up to 1 h)	200°C
In service temperature range	-40 to 80 °C
Glass transition temperature (Tg) DMTA 10 Hz, 2 K/min	-17 °C

PRELIMINARY STATEMENT

Prior to application it is necessary to read the **Safety Data Sheet** for information about precautionary measures and safety recommendations. Also, for chemical products exempt from compulsory labeling, the relevant precautions should always be observed.

APPLICATION

TEROSON RB 3216 is applied from pails or drums using high pressure pumps with a compression ratio minimum 50:1. For the best application the use of volume controlled dispensers is preferred. The heated application pistol can be used either manually or on a fixed jig. More commonly is attached to an automatic application system (robot, CNC). It is recommended to switch off heating during a shutdown of more than 1 hour. The pressure should be switched off after 15 minutes of non-production. Independent heating circuits should have the lowest temperature at the follower plate and the highest temperature at the application nozzle. To ensure an optimal wetting to the substrate TEROSON RB 3216 should be applied at elevated temperatures. After assembly of parts, the open time before curing is at least 4 weeks (indoor under storage conditions of maximum 30°C and 70% of humidity).The material is applied directly to oily sheet metal no more than 3 g/m² . If required, we will provide you with the additional information on suitable application equipment.

Recommended material temperature:

Follower plate and pump:	25 to 35 °C
Temperature at nozzle:	35 to 60 °C

CURING

TEROSON RB 3216 is cured while passing the EC oven, e.g. 25 minutes at 175 °C. The minimum curing cycle is 25 min at 170 °C. These are effective metal temperatures.

CLEANING

Fresh, uncured material can be removed with the aid of ethylacetate or gasoline. Cured adhesive can only be removed mechanically.

Henkel

Technical Data Sheet

TEROSON RB 3216

December 2013

STORAGE

Frost sensitive	no
Recommended storage temperature	5 to 25 °C
Shelf life	6 months

Disclaimer

Note:

The information provided in this Technical Data Sheet (TDS) including the recommendations for use and application of the product are based on our knowledge and experience of the product as at the date of this TDS. The product can have a variety of different applications as well as differing application and working conditions in your environment that are beyond our control. Henkel is, therefore, not liable for the suitability of our product for the production processes and conditions in respect of which you use them, as well as the intended applications and results. We strongly recommend that you carry out your own prior trials to confirm such suitability of our product.

Any liability in respect of the information in the Technical Data Sheet or any other written or oral recommendation(s) regarding the concerned product is excluded, except if otherwise explicitly agreed and except in relation to death or personal injury caused by our negligence and any liability under any applicable mandatory product liability law.

In case products are delivered by Henkel Belgium NV, Henkel Electronic Materials NV, Henkel Nederland BV, Henkel Technologies France SAS and Henkel France SA please additionally note the following:

In case Henkel would be nevertheless held liable, on whatever legal ground, Henkel's liability will in no event exceed the amount of the concerned delivery.

In case products are delivered by Henkel Colombiana, S.A.S. the following disclaimer is applicable:

The information provided in this Technical Data Sheet (TDS) including the recommendations for use and application of the product are based on our knowledge and experience of the product as at the date of this TDS. Henkel is, therefore, not liable for the suitability of our product for the production processes and conditions in respect of which you use them, as well as the intended applications and results. We strongly recommend that you carry out your own prior trials to confirm such suitability of our product.

Any liability in respect of the information in the Technical Data Sheet or any other written or oral recommendation(s) regarding the concerned product is excluded, except if otherwise explicitly agreed and except in relation to death or personal injury caused by our negligence and any liability under any applicable mandatory product liability law.

In case products are delivered by Henkel Corporation, Resin Technology Group, Inc., or Henkel Canada Corporation, the following disclaimer is applicable:

The data contained herein are furnished for information only and are believed to be reliable. We cannot assume responsibility for the results obtained by others over whose methods we have no control. It is the user's responsibility to determine suitability for the user's purpose of any production methods mentioned herein and to adopt such precautions as may be advisable for the protection of property and of persons against any hazards that may be involved in the handling and use thereof. In light of the foregoing, **Henkel Corporation specifically disclaims all warranties expressed or implied, including warranties of merchantability or fitness for a particular purpose, arising from sale or use of Henkel Corporation's products. Henkel Corporation specifically disclaims any liability for consequential or incidental damages of any kind, including lost profits.** The discussion herein of various processes or compositions is not to be interpreted as representation that they are free from domination of patents owned by others or as a license under any Henkel Corporation patents that may cover such processes or compositions. We recommend that each prospective user test his proposed application before repetitive use, using this data as a guide. This product may be covered by one or more United States or foreign patents or patent applications.

Trademark usage

Except as otherwise noted, all trademarks in this document are trademarks of Henkel Corporation in the U.S. and elsewhere. ® denotes a trademark registered in the U.S. Patent and Trademark Office.

Henkel AG & Co. KGaA
D-40191 Düsseldorf. Germany
Phone: +49-211-797-0
www.henkel.com

Henkel Central Eastern Europe GmbH
A-1030 Wien. Austria
Phone: +43-1711-040
www.henkel.com

Henkel & Cie AG
CH-4133 Pratteln. Switzerland
Phone: +41-61-825-7000
www.henkel.com

Safety Data Sheet

Revision Number: 001.2

Issue date: 12/27/2017

1. PRODUCT AND COMPANY IDENTIFICATION

Product name: **TEROSON RB 3216 known as TEROSTAT 3216 PA 25 KG**
Product type: Sealant
Restriction of Use: None identified
Company address:
Henkel Corporation
One Henkel Way
Rocky Hill, Connecticut 06067

IDH number: 1378570
Region: United States
Contact information:
Telephone: (860) 571-5100
MEDICAL EMERGENCY Phone: Poison Control Center
1-877-671-4608 (toll free) or 1-303-592-1711
TRANSPORT EMERGENCY Phone: CHEMTREC
1-800-424-9300 (toll free) or 1-703-527-3887
Internet: www.henkelna.com

2. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

DANGER: CAUSES SKIN IRRITATION.
MAY CAUSE AN ALLERGIC SKIN REACTION.
CAUSES SERIOUS EYE DAMAGE.
MAY CAUSE ALLERGY OR ASTHMA SYMPTOMS OR BREATHING DIFFICULTIES IF INHALED.

HAZARD CLASS	HAZARD CATEGORY
SKIN IRRITATION	2
SERIOUS EYE DAMAGE	1
RESPIRATORY SENSITIZATION	1
SKIN SENSITIZATION	1

PICTOGRAM(S)

Precautionary Statements

Prevention: Avoid breathing vapors, mist, or spray. Wash affected area thoroughly after handling. Contaminated work clothing should not be allowed out of the workplace. Wear protective gloves, eye protection, and face protection. In case of inadequate ventilation wear respiratory protection.

Response: IF ON SKIN: Wash with plenty of water. IF INHALED: If breathing is difficult, remove victim to fresh air and keep at rest in a position comfortable for breathing. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. If skin irritation or rash occurs: Get medical attention. If experiencing respiratory symptoms: Call a poison center or physician. Take off contaminated clothing.

Storage: Not prescribed

Disposal: Dispose of contents and/or container according to Federal, State/Provincial and local governmental regulations.

Classification complies with OSHA Hazard Communication Standard (29 CFR 1910.1200) and is consistent with the provisions of the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

See Section 11 for additional toxicological information.

3. COMPOSITION / INFORMATION ON INGREDIENTS

Hazardous Component(s)	CAS Number	Percentage*
Calcium carbonate	471-34-1	40 - 50
Calcium oxide	1305-78-8	1 - 5
Zinc oxide	1314-13-2	1 - 5
Di(benzothiazol-2-yl) disulphide	120-78-5	1 - 5
Distillates (petroleum), solvent-refined light paraffinic	64741-89-5	1 - 5
Sulfur	7704-34-9	1 - 5
Phenol-formaldehyde polymer	9003-35-4	1 - 5
Carbon black	1333-86-4	0.1 - 1
Methenamine	100-97-0	0.1 - 1

* Exact percentages may vary or are trade secret. Concentration range is provided to assist users in providing appropriate protections.

4. FIRST AID MEASURES

Inhalation:	If inhaled, immediately remove the affected person to fresh air. If symptoms develop and persist, get medical attention.
Skin contact:	Immediately wash skin thoroughly with soap and water. If symptoms develop and persist, get medical attention.
Eye contact:	In case of contact with the eyes, rinse immediately with plenty of water for 15 minutes, and seek immediate medical attention.
Ingestion:	Get immediate medical attention. Do not induce vomiting.
Symptoms:	See Section 11.
Notes to physician:	Treat symptomatically and supportively.

5. FIRE FIGHTING MEASURES

Extinguishing media:	Water spray (fog), foam, dry chemical or carbon dioxide.
Special firefighting procedures:	Wear full protective clothing. Wear self-contained breathing apparatus.
Unusual fire or explosion hazards:	May liberate large quantities of dense, foul-smelling smoke which may contain unidentified toxic gasses.
Hazardous combustion products:	Upon decomposition, this product emits carbon monoxide, carbon dioxide and/or low molecular weight hydrocarbons. Oxides of nitrogen.

6. ACCIDENTAL RELEASE MEASURES

Use personal protection recommended in Section 8, isolate the hazard area and deny entry to unnecessary and unprotected personnel.

Environmental precautions:	Prevent further leakage or spillage if safe to do so. Wear appropriate protective equipment and clothing during clean-up. Do not allow product to enter sewer or waterways.
Clean-up methods:	Absorb spill with inert material. Shovel material into appropriate container for disposal. Dispose of according to Federal, State and local governmental regulations.

TEROSON

Technical Data Sheet

TEROSON RB 3208 PA-25

December 2016

PRODUCT DESCRIPTION:

Technology	Rubber
Product Type	Antiflutter Adhesive

TEROSON RB 3208 PA-25 is a heat curing, solvent free, one component adhesive, based on rubbers. Special viscosity of the product leads to an excellent sag resistance and makes it wash-off resistant against aqueous cleaning and pretreatment agents. TEROSON RB 3208 PA-25 adheres well to oily steel sheets, aluminum and zinc coated surfaces. The cured material shows a foamy structure, is highly flexible and little dependent of changes in temperature. TEROSON RB 3208 PA-25 chemically cross-links at temperatures above 140 °C. Due to the good compatibility to E-coat paint it offers a safe corrosion protection even at boundary areas. TEROSON RB 3208 PA-25 can be painted after curing.

APPLICATION AREAS:

TEROSON RB 3208 PA-25 is used as antiflutter in the automotive body shop and shows good adhesion on oily surfaces. Low hardness prevents read-through effects. It is recommended for use, when wash-off resistance must be obtained without pre-gelling or pre-curing, and where a high degree of elasticity is required over a wide temperature range.

TECHNICAL DATA:
(Typical Test Results)

Uncured	
Colour	black
Density	approx. 1.5 g/cm³
Consistency	pasty
Viscosity (DIN 54458)	180 Pa.s
Equipment	P/P 25 mm
Frequency	10 Hz
Deformation	10 %
Temperature	45 °C
Cured (25 min. at 175 °C)	
Material Data (ISO 527-3)	
E-Modulus	approx. 3.5 MPa
Poisson ratio	approx. 0.36
Expansion rate	approx. 30 %
Shear strength (DIN EN 1465)	approx. 0.4 MPa
bonding area	25 x 20 mm
layer thickness	4 mm
substrate	HDG / EGS 0.75 mm
Temperature resistance	
short exposure (up to 1 h)	200 °C
In service temperature range	- 40 to 80 °C

PRELIMINARY STATEMENT

Prior to application it is necessary to read the **Safety Data Sheet** for information about precautionary measures and safety recommendations. Also, for chemical products exempt from compulsory labeling, the relevant precautions should always be observed.

APPLICATION

TEROSON RB 3208 PA-25 is applied from pails or drums using high pressure pumps with a compression ratio minimum 50:1. For the best application the use of volume controlled dispensers is preferred. The heated application pistol can be used either manually or on a fixed jig. More commonly is attached to an automatic application system (robot, CNC). It is recommended to switch off heating during a shutdown of more than 1 hour. The pressure should be switched off after 15 minutes of non-production. Independent heating circuits should have the lowest temperature at the follower plate and the highest temperature at the application nozzle. To ensure an optimal wetting to the substrate TEROSON RB 3208 PA-25 should be applied at elevated temperatures. After assembly of parts, the open time before curing is at least weeks (indoor under storage conditions of maximum °C and % of humidity).The material is applied directly to oily sheet metal no more than 3 g/m². If required, we will provide you with the additional information on suitable application equipment.

Recommended material temperature:

Follower plate and pump:	15 to 35 °C
Temperature at nozzle:	35 to 60 °C

CURING

TEROSON RB 3208 PA-25 is cured while passing the EC oven, e.g. 15 minutes at 175 °C. The minimum curing cycle is 15 min at 170 °C. These are effective metal temperatures.

CLEANING

Fresh, uncured material can be removed with the aid of ethylacetate or gasoline. Cured adhesive can only be removed mechanically.

Henkel

TEROSON RB 3208 PA-25

December 2016

STORAGE:

Frost sensitive	no
Recommended storage temperature	5 to 25 °C
Shelf life	6 months

Disclaimer

Note:
The information provided in this Technical Data Sheet (TDS) including the recommendations for use and application of the product are based on our knowledge and experience of the product as at the date of this TDS. The product can have a variety of different applications as well as differing application and working conditions in your environment that are beyond our control. Henkel is, therefore, not liable for the suitability of our product for the production processes and conditions in respect of which you use them, as well as the intended applications and results. We strongly recommend that you carry out your own prior trials to confirm such suitability of our product.
Any liability in respect of the information in the Technical Data Sheet or any other written or oral recommendation(s) regarding the concerned product is excluded, except if otherwise explicitly agreed and except in relation to death or personal injury caused by our negligence and any liability under any applicable mandatory product liability law.

In case products are delivered by Henkel Belgium NV, Henkel Electronic Materials NV, Henkel Nederland BV, Henkel Technologies France SAS and Henkel France SA please additionally note the following:
In case Henkel would be nevertheless held liable, on whatever legal ground, Henkel's liability will in no event exceed the amount of the concerned delivery.

In case products are delivered by Henkel Colombiana, S.A.S. the following disclaimer is applicable:
The information provided in this Technical Data Sheet (TDS) including the recommendations for use and application of the product are based on our knowledge and experience of the product as at the date of this TDS. Henkel is, therefore, not liable for the suitability of our product for the production processes and conditions in respect of which you use them, as well as the intended applications and results. We strongly recommend that you carry out your own prior trials to confirm such suitability of our product.
Any liability in respect of the information in the Technical Data Sheet or any other written or oral recommendation(s) regarding the concerned product is excluded, except if otherwise explicitly agreed and except in relation to death or personal injury caused by our negligence and any liability under any applicable mandatory product liability law.

In case products are delivered by Henkel Corporation, Resin Technology Group, Inc., or Henkel Canada Corporation, the following disclaimer is applicable:
The data contained herein are furnished for information only and are believed to be reliable. We cannot assume responsibility for the results obtained by others over whose methods we have no control. It is the user's responsibility to determine suitability for the user's purpose of any production methods mentioned herein and to adopt such precautions as may be advisable for the protection of property and of persons against any hazards that may be involved in the handling and use thereof. In light of the foregoing, **Henkel Corporation specifically disclaims all warranties expressed or implied, including warranties of merchantability or fitness for a particular purpose, arising from sale or use of Henkel Corporation's products. Henkel Corporation specifically disclaims any liability for consequential or incidental damages of any kind, including lost profits.** The discussion herein of various processes or compositions is not to be interpreted as representation that they are free from domination of patents owned by others or as a license under any Henkel Corporation patents that may cover such processes or compositions. We recommend that each prospective user test his proposed application before repetitive use, using this data as a guide. This product may be covered by one or more United States or foreign patents or patent applications.

Trademark usage: [Except as otherwise noted] All trademarks in this document are trademarks and/or registered trademarks of Henkel and its affiliates in the U.S. and elsewhere.

Henkel AG & Co. KGaA
D-40191 Düsseldorf. Germany
Phone: +49-211-797-0
www.henkel.com

Henkel Central Eastern Europe GmbH
A-1030 Wien. Austria
Phone: +43-1711-040
www.henkel.com

Henkel & Cie AG
CH-4133 Pratteln. Switzerland
Phone: +41-61-825-7000
www.henkel.com

Safety Data Sheet

Revision Number: 001.0

Issue date: 07/14/2016

1. PRODUCT AND COMPANY IDENTIFICATION

Product name: **TEROSON RB 3208 PA-25 known as TEROSTAT 3208PA-25 FA270**
IDH number: 1640442
Product type: adhesive and sealant
Restriction of Use: None identified
Region: United States
Company address:
Henkel AG & Co. KGaA
Henkelstr. 67
Düsseldorf 40589
Contact information:
Telephone: +49 (211) 797 0

2. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW	
DANGER:	CAUSES SKIN IRRITATION. MAY CAUSE AN ALLERGIC SKIN REACTION. CAUSES SERIOUS EYE DAMAGE. MAY CAUSE ALLERGY OR ASTHMA SYMPTOMS OR BREATHING DIFFICULTIES IF INHALED.

HAZARD CLASS	HAZARD CATEGORY
SKIN IRRITATION	2
SERIOUS EYE DAMAGE	1
RESPIRATORY SENSITIZATION	1
SKIN SENSITIZATION	1

PICTOGRAM(S)

Precautionary Statements

Prevention:	Avoid breathing dust or fumes. Wash affected area thoroughly after handling. Contaminated work clothing should not be allowed out of the workplace. Wear protective gloves, eye protection, and face protection. In case of inadequate ventilation wear respiratory protection.
Response:	IF ON SKIN: Wash with plenty of water. IF INHALED: If breathing is difficult, remove victim to fresh air and keep at rest in a position comfortable for breathing. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. If skin irritation or rash occurs: Get medical attention. If experiencing respiratory symptoms: Call a poison center or physician. Take off contaminated clothing.
Storage:	Not prescribed
Disposal:	Dispose of contents and/or container according to Federal, State/Provincial and local governmental regulations.

Classification complies with OSHA Hazard Communication Standard (29 CFR 1910.1200) and is consistent with the provisions of the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

See Section 11 for additional toxicological information.

3. COMPOSITION / INFORMATION ON INGREDIENTS

Hazardous Component(s)	CAS Number	Percentage*
Limestone	1317-65-3	30 - 60
Distillates (petroleum), solvent-refined light paraffinic	64741-89-5	10 - 30
Calcium carbonate	471-34-1	10 - 30
Calcium oxide	1305-78-8	1 - 5
Carbon black	1333-86-4	1 - 5
Zinc oxide	1314-13-2	0.1 - 1
Phthalic anhydride	85-44-9	0.1 - 1

* Exact percentage is a trade secret. Concentration range is provided to assist users in providing appropriate protections.

4. FIRST AID MEASURES

Inhalation:	If mist or vapor of this product is inhaled, remove person immediately to fresh air. Seek medical attention if symptoms develop or persist.
Skin contact:	Immediately wash skin thoroughly with soap and water. Obtain medical attention if irritation persists.
Eye contact:	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
Ingestion:	Rinse the mouth. Drink 1-2 glasses of water. Do not induce vomiting. Get immediate medical attention.
Symptoms:	See Section 11.

5. FIRE FIGHTING MEASURES

Extinguishing media:	Water spray (fog), foam, dry chemical or carbon dioxide.
Special firefighting procedures:	Wear full protective clothing. Wear self-contained breathing apparatus.
Unusual fire or explosion hazards:	None identified.
Hazardous combustion products:	Irritating and/or toxic fumes and gases may be emitted upon the product's decomposition.

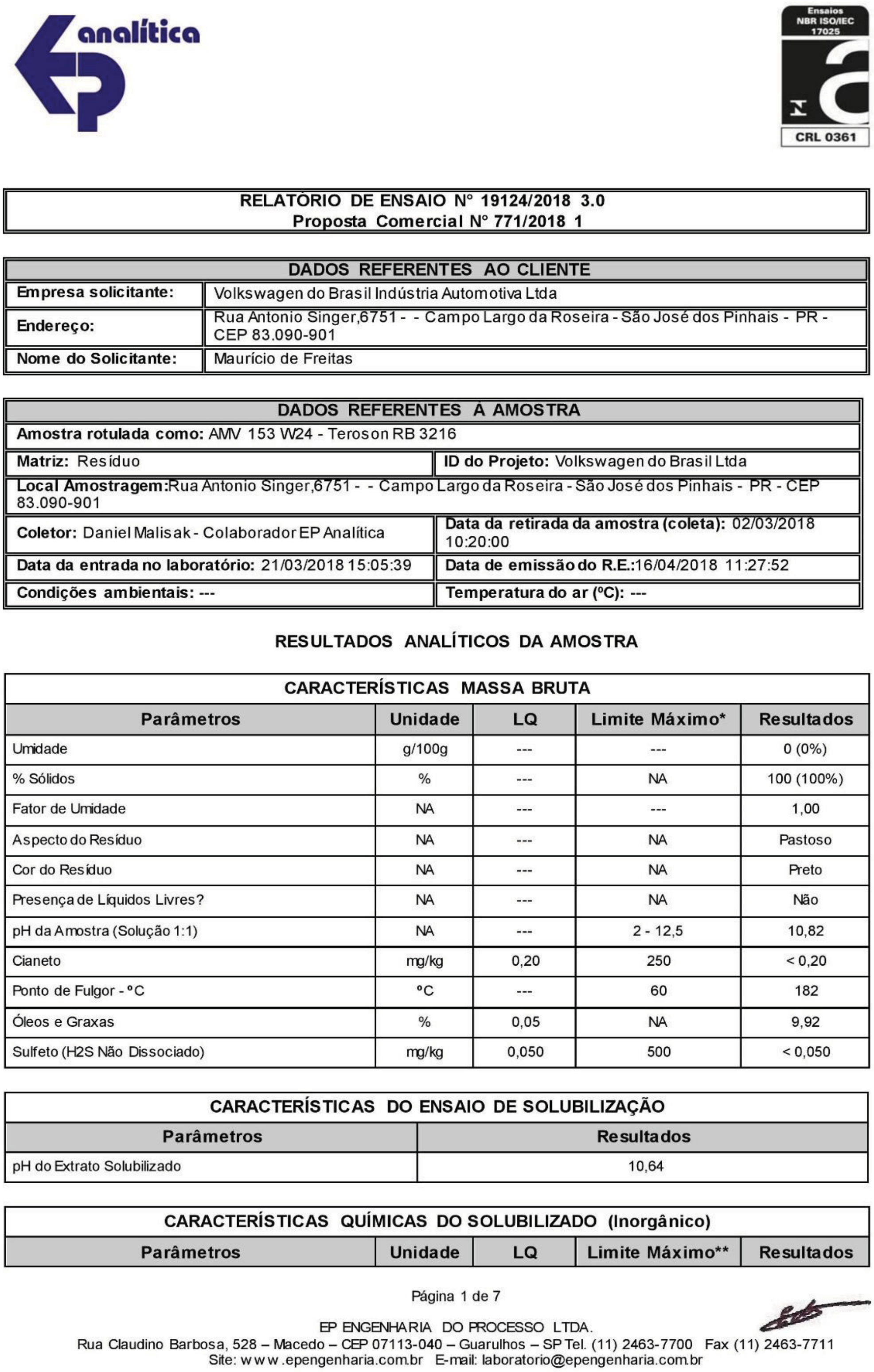
6. ACCIDENTAL RELEASE MEASURES

Use personal protection recommended in Section 8, isolate the hazard area and deny entry to unnecessary and unprotected personnel.

Environmental precautions:	Prevent further leakage or spillage if safe to do so. Wear suitable protective clothing, gloves and eye/face protection. Do not allow product to enter sewer or waterways. Remove all sources of ignition.
Clean-up methods:	Absorb spill with inert material. Shovel material into appropriate container for disposal. Dispose of according to Federal, State and local governmental regulations.

ANNEX 2

RESULTS OF SOLUBILITY AND LEACHING TESTS



Ensaios NBR ISO/IEC 17025
CRL 0361

RELATÓRIO DE ENSAIO N° 19124/2018 3.0 Proposta Comercial N° 771/2018 1

DADOS REFERENTES AO CLIENTE	
Empresa solicitante:	Volkswagen do Brasil Indústria Automotiva Ltda
Endereço:	Rua Antonio Singer,6751 - - Campo Largo da Roseira - São José dos Pinhais - PR - CEP 83.090-901
Nome do Solicitante:	Maurício de Freitas

DADOS REFERENTES À AMOSTRA	
Amostra rotulada como: AMV 153 W24 - Teroson RB 3216	
Matriz: Resíduo	**ID do Projeto:** Volkswagen do Brasil Ltda
Local Amostragem: Rua Antonio Singer,6751 - - Campo Largo da Roseira - São José dos Pinhais - PR - CEP 83.090-901	
Coletor: Daniel Malisak - Colaborador EP Analítica	**Data da retirada da amostra (coleta):** 02/03/2018 10:20:00
Data da entrada no laboratório: 21/03/2018 15:05:39	**Data de emissão do R.E.:**16/04/2018 11:27:52
Condições ambientais: ---	**Temperatura do ar (ºC):** ---

RESULTADOS ANALÍTICOS DA AMOSTRA

CARACTERÍSTICAS MASSA BRUTA

Parâmetros	Unidade	LQ	Limite Máximo*	Resultados
Umidade	g/100g	---	---	0 (0%)
% Sólidos	%	---	NA	100 (100%)
Fator de Umidade	NA	---	---	1,00
Aspecto do Resíduo	NA	---	NA	Pastoso
Cor do Resíduo	NA	---	NA	Preto
Presença de Líquidos Livres?	NA	---	NA	Não
pH da Amostra (Solução 1:1)	NA	---	2 - 12,5	10,82
Cianeto	mg/kg	0,20	250	< 0,20
Ponto de Fulgor - °C	°C	---	60	182
Óleos e Graxas	%	0,05	NA	9,92
Sulfeto (H2S Não Dissociado)	mg/kg	0,050	500	< 0,050

CARACTERÍSTICAS DO ENSAIO DE SOLUBILIZAÇÃO

Parâmetros	Resultados
pH do Extrato Solubilizado	10,64

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Inorgânico)

Parâmetros	Unidade	LQ	Limite Máximo**	Resultados

RELATORIO DE ENSAIO N° 19124/2018 3.0
Proposta Comercial N° 771/2018 1

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Inorgânico)

Parâmetros	Unidade	LQ	Limite Máximo**	Resultados
Alumínio	mg/L	0,010	0,2	0,040
Arsênio	mg/L	0,010	0,01	< 0,010
Bário	mg/L	0,010	0,7	< 0,010
Cádmio	mg/L	0,001	0,005	< 0,001
Chumbo	mg/L	0,010	0,01	< 0,010
Cianeto	mg/L	0,02	0,07	< 0,02
Cloreto	mg/L	0,20	250,0	0,72
Cobre	mg/L	0,009	2,0	< 0,009
Cromo Total	mg/L	0,010	0,05	< 0,010
Ferro	mg/L	0,010	0,3	< 0,010
Fluoreto	mg/L	0,20	1,5	< 0,20
Manganês	mg/L	0,010	0,1	< 0,010
Mercúrio	mg/L	0,0002	0,001	< 0,0002
Nitrato	mg/L	0,20	10,0	< 0,20
Prata	mg/L	0,010	0,05	< 0,010
Selênio	mg/L	0,010	0,01	< 0,010
Sódio	mg/L	0,500	200,0	1,09
Sulfato	mg/L	0,20	250,0	0,29
Surfactantes	mg/L	0,15	0,5	< 0,15
Zinco	mg/L	0,010	5,0	0,024

Obs: Ensaio conforme ABNT NBR 10006/2004 - "Procedimentos para obtenção de extrato solubilizado de resíduos sólidos"

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Orgânico)

Parâmetros	Unidade	LQ	Limite Máximo**	Resultados
2,4-D	mg/L	0,000050	0,03	< 0,000050
2,4,5-T	mg/L	0,000050	0,002	< 0,000050
2,4,5-TP (Silvex)	mg/L	0,000050	0,03	< 0,000050
Aldrin + Dieldrin	mg/L	0,000003	0,00003	< 0,000003
Clordanos	mg/L	0,000005	0,0002	< 0,000005
DDT(DDT + DDD + DDE)	mg/L	0,000001	0,002	< 0,000001
Endrin	mg/L	0,000003	0,0006	< 0,000003
Heptacloro + Heptacloro Epóxido	mg/L	0,000005	0,00003	< 0,000005

RELATORIO DE ENSAIO N° 19124/2018 3.0
Proposta Comercial N° 771/2018 1

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Orgânico)

Parâmetros	Unidade	LQ	Limite Máximo**	Resultados
Hexaclorobenzeno	mg/L	0,000005	0,001	< 0,000005
Lindano (g-BHC)	mg/L	0,000003	0,002	< 0,000003
Metoxicloro	mg/L	0,000010	0,02	< 0,000010
Toxafeno	mg/L	0,000010	0,005	< 0,000010
Fenóis	mg/L	0,000500	0,01	0,017490

Obs: Ensaio conforme ABNT NBR 10006/2004 - "Procedimentos para obtenção de extrato solubilizado de resíduos sólidos"

CARACTERÍSTICAS DO ENSAIO DE LIXIVIAÇÃO

Parâmetros	Resultados
pH da Amostra (Solução 5%)	4,80
Quantidade de Amostra Lixiviada (g)	100
Volume dos Líquidos (mL)	2000
Tempo Total de Lixiviação ± (hs)	18
pH do Extrato Lixiviado	4,89
pH da Amostra (Solução 50%)	4,84

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Inorgânico)

Parâmetros	Unidade	LQ	Limite Máximo***	Resultados
Arsênio	mg/L	0,010	1,0	< 0,010
Bário	mg/L	0,010	70,0	< 0,010
Cádmio	mg/L	0,001	0,5	< 0,001
Chumbo	mg/L	0,010	1,0	< 0,010
Cromo Total	mg/L	0,010	5,0	< 0,010
Fluoreto	mg/L	0,40	150,0	< 0,40
Mercúrio	mg/L	0,010	0,1	< 0,010
Prata	mg/L	0,010	5,0	< 0,010
Selênio	mg/L	0,010	1,0	< 0,010

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Orgânicos)

Parâmetros	Unidade	LQ	Limite Máximo***	Resultados
1,1-Dicloroeteno	mg/L	0,005	3,0	< 0,005
1,2-Dicloroetano	mg/L	0,005	1,0	< 0,005

RELATORIO DE ENSAIO N° 19124/2018 3.0
Proposta Comercial N° 771/2018 1

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Orgânicos)				
Parâmetros	**Unidade**	**LQ**	**Limite Máximo*****	**Resultados**
1,4-Diclorobenzeno	mg/L	0,005	7,5	< 0,005
2,4-D	mg/L	0,000050	3,0	< 0,000050
2,4-Dinitrotolueno	mg/L	0,000025	0,13	< 0,000025
2,4,5-T	mg/L	0,000050	0,2	< 0,000050
2,4,5-TP (Silvex)	mg/L	0,000050	1,0	< 0,000050
2,4,5-Triclorofenol	mg/L	0,000010	400,0	< 0,000010
2,4,6-Triclorofenol	mg/L	0,000010	20,0	< 0,000010
Aldrin + Dieldrin	mg/L	0,000003	0,003	< 0,000003
Benzeno	mg/L	0,005	0,5	< 0,005
Benzo(a)pireno	mg/L	0,000005	0,07	< 0,000005
Clordanos	mg/L	0,000005	0,02	< 0,000005
Cloreto de Vinila	mg/L	0,005	0,5	< 0,005
(Mono)Clorobenzeno	mg/L	0,005	100	< 0,005
Clorofórmio (Triclorometano)	mg/L	0,005	6,0	< 0,005
Cresóis	mg/L	0,000020	200,0	0,000187
DDT(DDT + DDD + DDE)	mg/L	0,000001	0,2	< 0,000001
Endrin	mg/L	0,000003	0,06	< 0,000003
Fenóis	ug/L	0,50	---	25
Heptacloro + Heptacloro Epóxido	mg/L	0,000005	0,003	< 0,000005
Hexaclorobenzeno	mg/L	0,000005	0,1	< 0,000005
Hexaclorobutadieno	mg/L	0,005	0,5	< 0,005
Hexacloroetano	mg/L	0,000100	3,0	< 0,000100
Lindano (g-BHC)	mg/L	0,000003	0,2	< 0,000003
m-Cresol	mg/L	0,000010	200,0	0,000147
Metiletilcetona	mg/L	0,500	200,0	< 0,500
Metoxicloro	mg/L	0,000010	2,0	< 0,000010
Nitrobenzeno	mg/L	0,000010	2,0	< 0,000010
o-Cresol	mg/L	0,000010	200,0	0,000040
p-Cresol	mg/L	0,000010	200,0	0,000147
Pentaclorofenol	mg/L	0,000050	0,9	< 0,000050
Piridina	mg/L	0,500	5,0	< 0,500

RELATORIO DE ENSAIO N° 19124/2018 3.0
Proposta Comercial N° 771/2018 1

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Orgânicos)				
Parâmetros	**Unidade**	**LQ**	**Limite Máximo*** **	**Resultados**
Toxafeno	mg/L	0,000010	0,5	< 0,000010
Tetracloreto de Carbono	mg/L	0,005	0,2	< 0,005
Tetracloroeteno	mg/L	0,005	4,0	< 0,005
Tricloroeteno	mg/L	0,005	7,0	< 0,005

Obs: Ensaio conforme ABNT NBR 10005/2004 - "Procedimentos para obtenção de extrato lixiviado de resíduos sólidos"

ENSAIOS DE RECUPERAÇÃO			
Compostos Surrogates	**Concentração Adicionada (mg/l)**	**Faixa de Recuperação (%)**	**Recuperação do Surrogate (%) Amostra**
Ytrio	0,08	80-120	95
Tolueno-d8	50	70-130	80
2-Fluorbifenil	500	30-130	37
Terfenil-d14	500	30-130	87
p-Bromofluorobenzeno	50	70-130	101
2-Fluorbifenil	500	30-130	54
Terfenil-d14	500	30-130	69
Ytrio	0,08	80-120	95

CLASSIFICAÇÃO

As opiniões e interpretações expressas abaixo não fazem parte do escopo da acreditação deste laboratório.

O resíduo é Classificado como Classe II A, não Inerte e não Perigoso conforme o item 4.2.2.1, segundo NBR 10004/04.

* **Limite Máximo** – Massa Bruta conforme ABNT NBR 10004/2004
** **Limite Máximo** – Solubilizado conforme ABNT NBR 10006/2004 (anexo G)
*** **Limite Máximo** – Lixiviado conforme ABNT NBR 10005/2004 (anexo F)

Legenda
LQ= Limite de Quantificação (pode variar de acordo com a interferência da matriz)
ND= Não Detectado
NA ou --- = Não Aplicável
VMP= Valor Máximo Permitido

Abrangência
O(s) resultado(s) apresentados possui(em) significação restrita e se aplica tão somente à(s) amostra(s) analisada(s).
Este Relatório de Ensaio só pode ser reproduzido por inteiro e sem nenhuma alteração. Reprodução parcial somente com

prévia autorização.

Amostragem
Caso a amostragem tenha sido realizada pela EP Analítica, o procedimento de coleta seguiu os critérios estabelecidos na Instrução Técnica IT 06-07.149.

Data de realização das análises
Para amostragem realizada pela EP Analítica, o prazo de execução das análises seguem o prazo de validade estabelecido pelo Standard Methods e/ou outra norma aplicável em sua última revisão.
Quando a amostragem é de responsabilidade do Cliente, qualquer desvio identificado na etapa de conferência é previamente informado ao cliente para a aprovação e continuidade do processo. Neste caso, a validade dos resultados dos ensaios pode ser afetada.

Plano de Amostragem
O plano de amostragem é de responsabilidade de quem efetuar a retirada de amostra (coleta).

Prazo de Retenção da(s) amostras(s)
A(s) amostra(s) tem um prazo de guarda de 15 dias corridos após a emissão do Relatório de Ensaio, exceto para a(s) amostra(s) perecível(is) – descarte imediato.

Massa Bruta

Parâmetro	**Norma e/ou Procedimento**
Cianeto	IT 06-07.70(B) rev.06
Umidade e % Sólidos	IT 06-07.52 rev.04
Sulfeto de Hidrogênio (H2S)	IT 06-07.20(B) rev.06
Óleos e Graxas	IT 06-07.133 rev.04

Lixiviado

Parâmetro	**Norma e/ou Procedimento**
VOC	IT 06-07.160 rev.03
Fluoreto	IT 06-07.16(A) rev.05
SVOC's	EPA Method 8270D
Metais	EPA 3005 A:1992

Solubilizado

Parâmetro	**Norma e/ou Procedimento**
Metais	IT 06-07.83 Rev.06
Cianeto	IT 06-07.70(B) rev.06
Surfactantes	IT 06-07.180 rev.01
SVOC's	EPA Method 8270D
Metais	EPA 3005 A:1992
Ânions	SMWW 4110 B, 4110 D

Signatários Autorizados
Edísio Pereira Figueiredo
Karina Cibele Oliveira
Marcelo Kazuo Takata

Edísio Pereira Figueiredo - Gerência Técnica - CRQ
04263329 - 4ª Região

Para verificação da autenticidade deste Relatório de Ensaio acesse o link: http://177.70.99.8/mylimsportal/Login e insira no campo indicado a "Chave de Validação" (Checksum): 07d6d1e8abc1f8f813d6ef51686aa24b

analítica

Ensaios NBR ISO/IEC 17025
CRL 0361

RELATORIO DE ENSAIO N° 19126/2018 3.0
Proposta Comercial N° 771/2018 1

DADOS REFERENTES AO CLIENTE	
Empresa solicitante:	Volkswagen do Brasil Indústria Automotiva Ltda
Endereço:	Rua Antonio Singer,6751 - - Campo Largo da Roseira - São José dos Pinhais - PR - CEP 83.090-901
Nome do Solicitante:	Maurício de Freitas

DADOS REFERENTES À AMOSTRA	
Amostra rotulada como: AKL 450 F40 - Teroson RB PA -25	
Matriz: Resíduo	**ID do Projeto:** Volkswagen do Brasil Ltda
Local Amostragem: Rua Antonio Singer,6751 - - Campo Largo da Roseira - São José dos Pinhais - PR - CEP 83.090-901	
Coletor: Daniel Malisak - Colaborador EP Analítica	**Data da retirada da amostra (coleta):** 02/03/2018 10:45:00
Data da entrada no laboratório: 21/03/2018 15:06:47	**Data de emissão do R.E.:** 16/04/2018 11:28:16
Condições ambientais: ---	**Temperatura do ar (ºC):** ---

RESULTADOS ANALÍTICOS DA AMOSTRA

CARACTERÍSTICAS MASSA BRUTA

Parâmetros	Unidade	LQ	Limite Máximo*	Resultados
Umidade	g/100g	---	---	0 (0%)
% Sólidos	%	---	NA	100 (100%)
Fator de Umidade	NA	---	---	1,00
Aspecto do Resíduo	NA	---	NA	Pastoso
Cor do Resíduo	NA	---	NA	Preto
Presença de Líquidos Livres?	NA	---	NA	Não
pH da Amostra (Solução 1:1)	NA	---	2 - 12,5	10,93
Cianeto	mg/kg	0,20	250	< 0,20
Ponto de Fulgor - °C	°C	---	60	186
Óleos e Graxas	%	0,05	NA	6,52
Sulfeto (H2S Não Dissociado)	mg/kg	0,050	500	< 0,050

CARACTERÍSTICAS DO ENSAIO DE SOLUBILIZAÇÃO

Parâmetros	Resultados
pH do Extrato Solubilizado	10,82

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Inorgânico)

Parâmetros	Unidade	LQ	Limite Máximo**	Resultados

RELATORIO DE ENSAIO N° 19126/2018 3.0
Proposta Comercial N° 771/2018 1

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Inorgânico)

Parâmetros	Unidade	LQ	Limite Máximo**	Resultados
Alumínio	mg/L	0,010	0,2	< 0,010
Arsênio	mg/L	0,010	0,01	< 0,010
Bário	mg/L	0,010	0,7	< 0,010
Cádmio	mg/L	0,001	0,005	< 0,001
Chumbo	mg/L	0,010	0,01	< 0,010
Cianeto	mg/L	0,02	0,07	< 0,02
Cloreto	mg/L	2,00	250,0	14,4
Cobre	mg/L	0,009	2,0	< 0,009
Cromo Total	mg/L	0,010	0,05	< 0,010
Ferro	mg/L	0,010	0,3	< 0,010
Fluoreto	mg/L	0,20	1,5	< 0,20
Manganês	mg/L	0,010	0,1	< 0,010
Mercúrio	mg/L	0,0002	0,001	< 0,0002
Nitrato	mg/L	0,20	10,0	< 0,20
Prata	mg/L	0,010	0,05	< 0,010
Selênio	mg/L	0,010	0,01	< 0,010
Sódio	mg/L	0,500	200,0	1,76
Sulfato	mg/L	2,00	250,0	3,50
Surfactantes	mg/L	0,15	0,5	3,08
Zinco	mg/L	0,010	5,0	< 0,010

Obs: Ensaio conforme ABNT NBR 10006/2004 - "Procedimentos para obtenção de extrato solubilizado de resíduos sólidos"

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Orgânico)

Parâmetros	Unidade	LQ	Limite Máximo**	Resultados
2,4-D	mg/L	0,000050	0,03	< 0,000050
2,4,5-T	mg/L	0,000050	0,002	< 0,000050
2,4,5-TP (Silvex)	mg/L	0,000050	0,03	< 0,000050
Aldrin + Dieldrin	mg/L	0,000003	0,00003	< 0,000003
Clordanos	mg/L	0,000005	0,0002	< 0,000005
DDT(DDT + DDD + DDE)	mg/L	0,000001	0,002	< 0,000001
Endrin	mg/L	0,000003	0,0006	< 0,000003
Heptacloro + Heptacloro Epóxido	mg/L	0,000005	0,00003	< 0,000005

CARACTERÍSTICAS QUÍMICAS DO SOLUBILIZADO (Orgânico)				
Parâmetros	**Unidade**	**LQ**	**Limite Máximo****	**Resultados**
Hexaclorobenzeno	mg/L	0,000005	0,001	< 0,000005
Lindano (g-BHC)	mg/L	0,000003	0,002	< 0,000003
Metoxicloro	mg/L	0,000010	0,02	< 0,000010
Toxafeno	mg/L	0,000010	0,005	< 0,000010
Fenóis	mg/L	0,000050	0,01	< 0,000050

Obs: Ensaio conforme ABNT NBR 10006/2004 - "Procedimentos para obtenção de extrato solubilizado de resíduos sólidos"

CARACTERÍSTICAS DO ENSAIO DE LIXIVIAÇÃO	
Parâmetros	**Resultados**
pH da Amostra (Solução 5%)	5,43
Quantidade de Amostra Lixiviada (g)	100
Volume dos Líquidos (mL)	2000
Tempo Total de Lixiviação ± (hs)	18
pH do Extrato Lixiviado	5,52
pH da Amostra (Solução 50%)	5,48

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Inorgânico)				
Parâmetros	**Unidade**	**LQ**	**Limite Máximo*****	**Resultados**
Arsênio	mg/L	0,010	1,0	< 0,010
Bário	mg/L	0,010	70,0	< 0,010
Cádmio	mg/L	0,001	0,5	< 0,001
Chumbo	mg/L	0,010	1,0	< 0,010
Cromo Total	mg/L	0,010	5,0	< 0,010
Fluoreto	mg/L	0,40	150,0	< 0,40
Mercúrio	mg/L	0,010	0,1	< 0,010
Prata	mg/L	0,010	5,0	< 0,010
Selênio	mg/L	0,010	1,0	< 0,010

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Orgânicos)				
Parâmetros	**Unidade**	**LQ**	**Limite Máximo*****	**Resultados**
1,1-Dicloroeteno	mg/L	0,005	3,0	< 0,005
1,2-Dicloroetano	mg/L	0,005	1,0	< 0,005

RELATORIO DE ENSAIO N° 19126/2018 3.0
Proposta Comercial N° 771/2018 1

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Orgânicos)				
Parâmetros	**Unidade**	**LQ**	**Limite Máximo*** **	**Resultados**
1,4-Diclorobenzeno	mg/L	0,005	7,5	< 0,005
2,4-D	mg/L	0,000050	3,0	< 0,000050
2,4-Dinitrotolueno	mg/L	0,000025	0,13	< 0,000025
2,4,5-T	mg/L	0,000050	0,2	< 0,000050
2,4,5-TP (Silvex)	mg/L	0,000050	1,0	< 0,000050
2,4,5-Triclorofenol	mg/L	0,000010	400,0	< 0,000010
2,4,6-Triclorofenol	mg/L	0,000010	20,0	< 0,000010
Aldrin + Dieldrin	mg/L	0,000003	0,003	< 0,000003
Benzeno	mg/L	0,005	0,5	< 0,005
Benzo(a)pireno	mg/L	0,000005	0,07	< 0,000005
Clordanos	mg/L	0,000005	0,02	< 0,000005
Cloreto de Vinila	mg/L	0,005	0,5	< 0,005
(Mono)Clorobenzeno	mg/L	0,005	100	< 0,005
Clorofórmio (Triclorometano)	mg/L	0,005	6,0	< 0,005
Cresóis	mg/L	0,000020	200,0	0,000216
DDT(DDT + DDD + DDE)	mg/L	0,000001	0,2	< 0,000001
Endrin	mg/L	0,000003	0,06	< 0,000003
Fenóis	ug/L	0,050	---	0,22
Heptacloro + Heptacloro Epóxido	mg/L	0,000005	0,003	< 0,000005
Hexaclorobenzeno	mg/L	0,000005	0,1	< 0,000005
Hexaclorobutadieno	mg/L	0,005	0,5	< 0,005
Hexacloroetano	mg/L	0,000100	3,0	< 0,000100
Lindano (g-BHC)	mg/L	0,000003	0,2	< 0,000003
m-Cresol	mg/L	0,000010	200,0	0,000216
Metiletilcetona	mg/L	0,500	200,0	< 0,500
Metoxicloro	mg/L	0,000010	2,0	< 0,000010
Nitrobenzeno	mg/L	0,000010	2,0	< 0,000010
o-Cresol	mg/L	0,000010	200,0	< 0,000010
p-Cresol	mg/L	0,000010	200,0	0,000216
Pentaclorofenol	mg/L	0,000050	0,9	< 0,000050
Piridina	mg/L	0,500	5,0	< 0,500

RELATORIO DE ENSAIO N° 19126/2018 3.0
Proposta Comercial N° 771/2018 1

CARACTERÍSTICAS QUÍMICAS DO LIXIVIADO (Orgânicos)				
Parâmetros	**Unidade**	**LQ**	**Limite Máximo*** **	**Resultados**
Toxafeno	mg/L	0,000010	0,5	< 0,000010
Tetracloreto de Carbono	mg/L	0,005	0,2	< 0,005
Tetracloroeteno	mg/L	0,005	4,0	< 0,005
Tricloroeteno	mg/L	0,005	7,0	< 0,005

Obs: Ensaio conforme ABNT NBR 10005/2004 - "Procedimentos para obtenção de extrato lixiviado de resíduos sólidos"

ENSAIOS DE RECUPERAÇÃO			
Compostos Surrogates	**Concentração Adicionada (mg/l)**	**Faixa de Recuperação (%)**	**Recuperação do Surrogate (%) Amostra**
Ytrio	0,08	80-120	95
Tolueno-d8	50	70-130	79
2-Fluorbifenil	500	30-130	87
Terfenil-d14	500	30-130	91
p-Bromofluorobenzeno	50	70-130	93
2-Fluorbifenil	500	30-130	45
Terfenil-d14	500	30-130	58
Ytrio	0,08	80-120	95

CLASSIFICAÇÃO

As opiniões e interpretações expressas abaixo não fazem parte do escopo da acreditação deste laboratório.

O resíduo é Classificado como Classe II A, não Inerte e não Perigoso conforme o item 4.2.2.1, segundo NBR 10004/04.

* **Limite Máximo** – Massa Bruta conforme ABNT NBR 10004/2004
** **Limite Máximo** – Solubilizado conforme ABNT NBR 10006/2004 (anexo G)
*** **Limite Máximo** – Lixiviado conforme ABNT NBR 10005/2004 (anexo F)

Legenda
LQ= Limite de Quantificação (pode variar de acordo com a interferência da matriz)
ND= Não Detectado
NA ou --- = Não Aplicável
VMP= Valor Máximo Permitido

Abrangência
O(s) resultado(s) apresentados possui(em) significação restrita e se aplica tão somente à(s) amostra(s) analisada(s).
Este Relatório de Ensaio só pode ser reproduzido por inteiro e sem nenhuma alteração. Reprodução parcial somente com

prévia autorização.

Amostragem
Caso a amostragem tenha sido realizada pela EP Analítica, o procedimento de coleta seguiu os critérios estabelecidos na Instrução Técnica IT 06-07.149.

Data de realização das análises
Para amostragem realizada pela EP Analítica, o prazo de execução das análses seguem o prazo de validade estabelecido pelo Standard Methods e/ou outra norma aplicável em sua última revisão.
Quando a amostragem é de responsabilidade do Cliente, qualquer desvio identificado na etapa de conferência é previamente informado ao cliente para a aprovação e continuidade do processo. Neste caso, a validade dos resultados dos ensaios pode ser afetada.

Plano de Amostragem
O plano de amostragem é de responsabilidade de quem efetuar a retirada de amostra (coleta).

Prazo de Retenção da(s) amostras(s)
A(s) amostra(s) tem um prazo de guarda de 15 dias corridos após a emissão do Relatório de Ensaio, exceto para a(s) amostra(s) perecível(is) – descarte imediato.

Massa Bruta

Parâmetro	Norma e/ou Procedimento
Cianeto	IT 06-07.70(B) rev.06
Umidade e % Sólidos	IT 06-07.52 rev.04
Sulfeto de Hidrogênio (H2S)	IT 06-07.20(B) rev.06
Óleos e Graxas	IT 06-07.133 rev.04

Lixiviado

Parâmetro	Norma e/ou Procedimento
VOC	IT 06-07.160 rev.03
Fluoreto	IT 06-07.16(A) rev.05
SVOC's	EPA Method 8270D
Metais	EPA 3005 A:1992

Solubilizado

Parâmetro	Norma e/ou Procedimento
Metais	IT 06-07.83 Rev.06
Cianeto	IT 06-07.70(B) rev.06
Surfactantes	IT 06-07.180 rev.01
SVOC's	EPA Method 8270D
Metais	EPA 3005 A:1992
Ânions	SMWW 4110 B, 4110 D

RELATORIO DE ENSAIO N° 19126/2018 3.0
Proposta Comercial N° 771/2018 1

Signatários Autorizados
Edísio Pereira Figueiredo
Karina Cibele Oliveira
Marcelo Kazuo Takata

Edísio Pereira Figueiredo - Gerência Técnica - CRQ
04263329 - 4ª Região

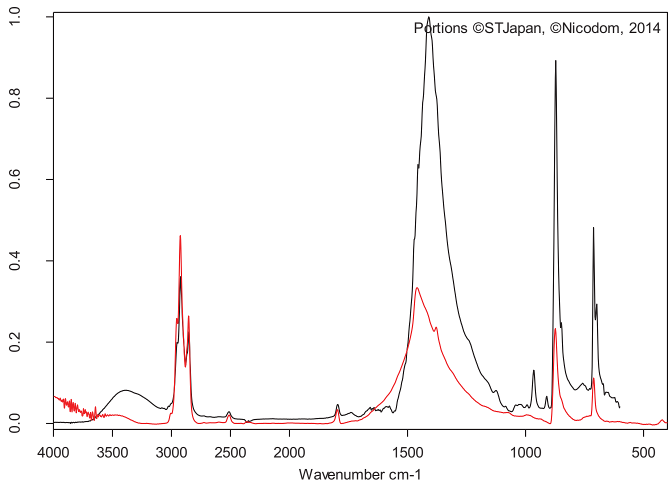
Para verificação da autenticidade deste Relatório de Ensaio acesse o link: http://177.70.99.8/mylimsportal/Login e insira no campo indicado a "Chave de Validação" (Checksum): ae66927bce6c7bad168c2142172a52bd

ANNEX 3

THE RESULTS OF THE FTIR SPECTRUM´S LIBRARY SEARCH AND ITS COMPARISON WITH THE FTIR SPECTRUM OF RESIDUES' SAMPLE.

Sample number (1): TEROSON RB 3208 PA-25

Search Library **25/06/2018 09:52:01**



Compound Name	RUBBER WHITE CACO3 FILLED
Molecular Formula	
Molecular Weight	
CAS Registry Number	
Sample Preparation	ATR single bounce
Comment	product
Reference	MP1600/ MP1600
Copyright	(c) 2014 Nicodom
Entry No.	159
Library name	ATR-LIB-POLYMERS-4-472-2.S01

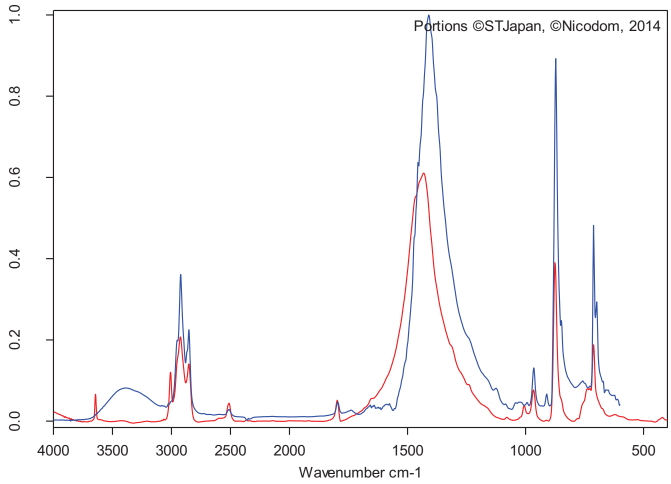
Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
⬛	302	RUBBER WHITE CACO3 FILLED			

Color	File	Path	Spectrum Type
🟥	AKLabsopus.0	D:	Query Spectrum

Page 1 of 1

Sample number (2): TEROSON RB 3216

Search Library **25/06/2018 09:55:45**



Compound Name	RUBBER WHITE CACO3 FILLED
Molecular Formula	
Molecular Weight	
CAS Registry Number	
Sample Preparation	ATR single bounce
Comment	product
Reference	MP1600/ MP1600
Copyright	(c) 2014 Nicodom
Entry No.	159
Library name	ATR-LIB-POLYMERS-4-472-2.S01

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
🟦	579	RUBBER WHITE CACO3 FILLED			

Color	File	Path	Spectrum Type
🟥	AMVabsopus.0	D:	Query Spectrum

Glossary

Rubber- a tough elastic polymeric substance made from the latex of a tropical plant or synthetically.

Resin- a solid or highly viscous substance of plant or synthetic origin that is typically convertible into polymers.

Plasticizer- a substance (typically a solvent) added to a synthetic resin to produce or promote plasticity and flexibility and to reduce brittleness.

Cross-link- a chemical bond between different chains of atoms in a polymer or other complex molecules.

Vulcanization- a chemical process for converting rubbers or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators. These additives modify the polymer by forming cross-links (bridges) between individual polymer chains.

Blowing Agent- a substance which is capable of producing a cellular structure via a foaming process in a variety of materials that undergo hardening or phase transition, such as polymers, plastics, and metals.

Thermosetting- denoting substances (plastics, polymers, and especially synthetic resins) that set permanently when heated.

Thermoplastic- denoting substances (plastics, polymers, and especially synthetic resins) that become plastic on heating and harden on cooling and are able to repeat these processes

Thermoset resin- a malleable solid or liquid material which trun into a plastic, or elastomer (rubber) by crosslinking.

Oligomer- An oligomer is a molecular complex of chemicals that consists of a few monomer units, in contrast to a polymer, where the number of monomers is, in principle, infinite.