DEVELOPMENT OF NATURAL RUBBER BASED COMPOUNDS FOR MANUFACTURE OF ABRASION RESISTANT GLOVES

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Degree of Master of Science

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Thesis submitted in partial fulfillment of the requirements for the degree Master of Science in Polymer Technology

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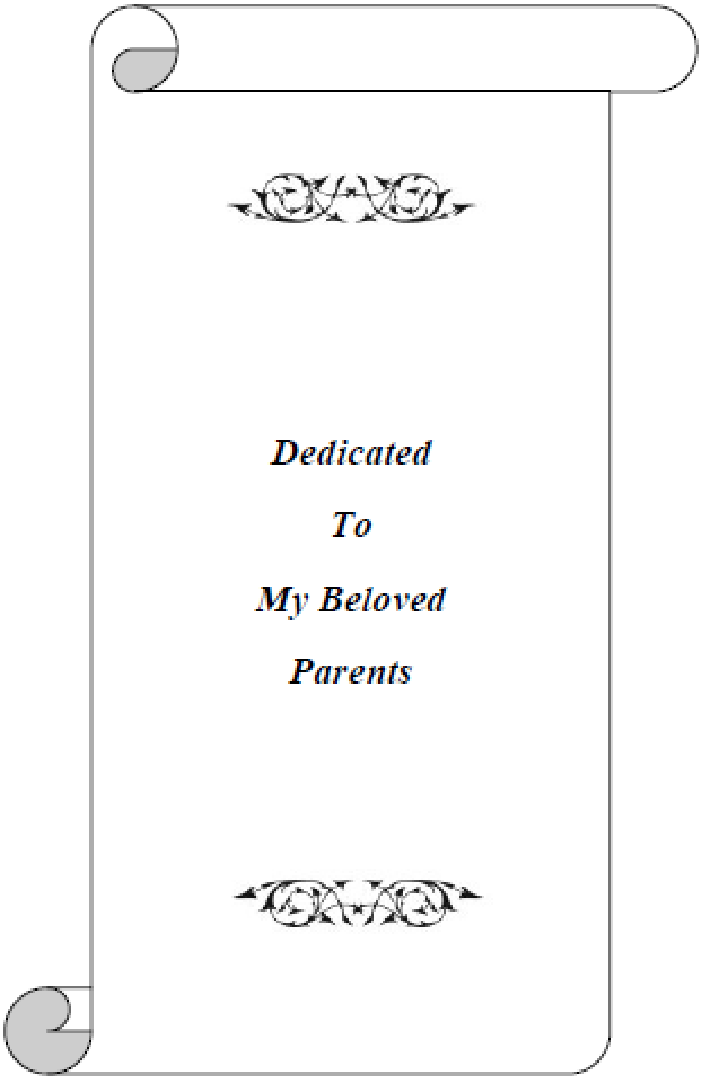

Dedicated

To

My Beloved

Parents

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ABSTRACT

Key words: Abrasion resistance, Fume silica, Silane Coupling agent

Industrial glove industry is a glooming industry which focuses performance enhancement with lowest possible cost. Abrasion resistance is one of the main performance indicators of an industrial glove. Abrasion resistance was improved in the study using reinforcing filler material and a coupling agent with a minimum cost.

Surfynol was selected as the best dispersion agent to couple with fume silica and precipitated silica from a range of dispersion agents. Both silica materials were optimized for loading level and fume silica was selected as the filler with most abrasion resistance. The optimized loading level for fume silica was 7 parts per hundred rubber. Silane was used as the coupling agent for the semi-reinforcing filler material and it was optimized as 0.5 parts per hundred rubber for the best abrasion performance.

The samples were tested and validated for abrasion resistance, tensile strength, cut resistance, tear resistance, puncture resistance, stiffness, grip and aging. Microscopic view of fume silica loaded glove sample was compared with that of calcium carbonate loaded glove sample and validated for subject of uniformity of coating layers.

Abrasion resistance was improved by using reinforcing filler fume silica instead of non-reinforcing filler calcium carbonate. Silane was used as the coupling agent and it was optimized for the best abrasion performance. This newly developed receipt helped to improve the abrasion resistance by 6 times compared to traditionally manufactured gloves out of natural rubber latex filled with non-reinforcing filler calcium carbonate.

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LIST OF ABBREVIATION

BOM- Bill of Material

DRC- Dry Rubber Content

EN- European Norms

ERP- Enterprise Resource Planning

MST- Mechanical Stability Time

PPE- Personal Protective Equipment

PVC- Polyvinyl Chloride

TSC- Total Solid Content

TSI- Toluene Swelling Index

VFA- Volatile Fatty Acid

1. INTRODUCTION

Abrasion phenomenon has been a subject of intensive study for years. In spite of a lot of publications available on this subject, abrasion phenomenon is not completely understood since viscoelasticity of polymers makes the analysis quite complicated.

There are many researches carried out for abrasion resistance improvement of polymer-based products, (Arayapranee, 2012; Association for contract textiles, 2011; Bauer, et al., 2002)in plastic industries, fabric coating industries, rubber-based product manufacturing industries, polymeric ink industries, garment industries and universities for special customer purposes and other research purposes. Most of the studies have focused on abrasion performance improvement related to dry rubber industry. As the most factors and processes are complex and complicated in liquid rubber industry, only a limited number of researches can be seen (NG , et al., 1994; Riyajan & Santipanusopon, 2010), In this context the present research focused on improving the abrasion resistance of industrial gloves.

Glove industry is a rapidly growing business and pioneers are more focusing on technological development as well as performance enhancement of the products. Other than that, commercial concerns such as cost reduction, operational efficiency improvements, legal compliance and regulation requirements fulfillment are also focused to have success in the business. This study will be advantageous even to industries, to improve abrasion resistant properties of natural rubber coated gloves, through the compound modification at lowest possible cost.

Further, based on industrial requirements, many rules & regulations, testing standards, sample selection criteria and product control for European customs, have been more stringent since April 2018. Abrasion resistance performance of gloves is also under this changed EN388:2016 “standard for protective gloves against mechanical risks”. Taking into consideration above said the results of the proposed research would be helpful in better understanding one of the most complex abrasion phenomenon from one side and from another side could be used by glove manufacturing industrialists to improve the abrasion performance of industrial gloves to reduce failures and risks.

2. OBJECTIVES

The objectives of the study were

1) Identification of the factors effecting on abrasion resistance of natural rubber-based gloves.
2) Estimation of the effect of reinforcement filler loading on abrasion performance of natural rubber based industrial gloves.
3) Optimization of fume silica filler material and Silane coupling agent material to develop a natural rubber-based compound for industrial glove application.
4) Determination of the mechanical performance of developed compound in natural rubber based industrial glove applications.

3. LITERATURE REVIEW

3.1.Gloves

The glove is a personal protective equipment (PPE) which protects the hand or a part of the hand against hazards such as physical, heat, chemical, electrical, biohazards or use for special activities such as medical purposes, food handling purposes, etc. The glove can be categorized in to four groups as shown is Figure 3.1 according to the way of manufacturing and material configuration.

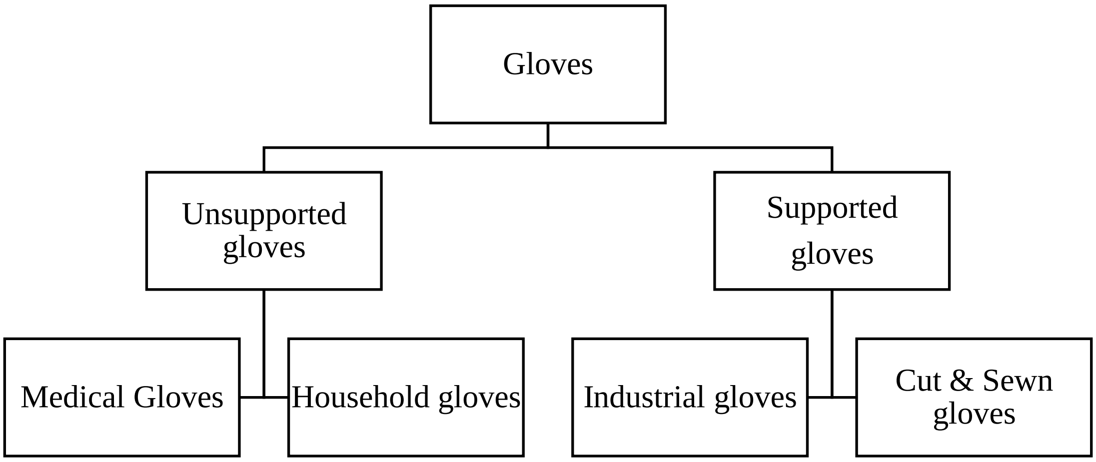


Figure 3.1-Glove Categorization format

Source: (Fontaine, 2019; Predolich, 2019)

Accordingly, gloves can be divided in to two major categories as supported and unsupported gloves based on availability of supportive liner. Supported gloves are made with cut and sewn or kitted fabric liner coated with polymeric materials such as latex, nitrile, PVC, silicone, neoprene, etc while unsupported gloves are made with polymeric materials itself, such as latex, nitrile, vinyl without having underneath lining (Predolich, 2019; safety Gear Pro, 2019).

Further, unsupported gloves can be divided in to two categories as Medical/ Disposable gloves or household gloves based on application and product characteristics. Supported gloves can be cascaded further in to two categories as industrial gloves and Cut and sewn gloves based on manufacturing process. Table 3.1 describes further details regarding four main types of gloves in personal protective industry (The Glove Company, 2019).

Table 3.1-Glove Characterization

Type of Gloves	Glove Characterization
Medical Gloves	Made with dipping ceramic formers with embossed grip patterns directly in polymers such as latex, nitrile, etc. Use for chemicals, biohazards, handling of potentially dangerous substances, contamination hazards, etc. Special characteristics are sterility and cleanliness of the glove.
House Hold Gloves	Made with latex, nitrile, and vinyl polymers Mainly use in disposable applications, such as food preparation, painting, household cleaning, and general purposes.
Industrial Gloves	Made with nitrile, latex, neoprene, silicone, and PVC Liner made with Cotton, Nylon, Polyester, Kevlar, Glass fiber, Acrylic, Dyneema, etc. Use in industrial high-risk applications such as heat, chemical, mechanical, fire, cold, cut hazards.
Cut & Sewn Gloves	Made with coated fabric, leather, thermo plastic rubber and fabric materials. Use in medium risk applications such as sports, assembly operations, etc.

3.2.Materials Used in Industrial Glove Manufacturing

Generally, gloves are made with polymeric materials such as natural rubber, chloroprene rubber, nitrile rubber, silicone rubber, poly vinyl chloride rubber, poly urethane rubber with or without supportive liner materials such as polyester, nylon, Kevlar, acrylic, cotton and other ingredients such as bonding agents, curing agents, coloring agents, etc. Mostly industrial gloves are made with supportive liner and coat on the liner with polymeric compound (EHS Today, 2000). Accordingly, basic raw materials which are used in natural rubber based industrial glove manufacturing process can be described as follows (Akabane, 2016).

3.2.1. Supportive liner

Most of the natural rubber based industrial gloves are used for general purpose applications and expected to have good mechanical performance with low cost. Therefore, most of natural rubber based industrial gloves for general purposes are made with nylon knitted liner or polyester knitted liner to reduce unit cost of gloves. However, advanced yarns or engineered yarns are used for high cut resistance, tear resistance, and puncture resistance applications (DPL Group, 2019).

3.2.2. Compound

Compound is a homogenous mixture of natural rubber latex and other ingredients which are used in natural rubber-based product manufacturing industry. Compounding ingredients are added in to the compound to obtain required physical properties of the final product, to obtain processing characteristics and to achieve required qualities of the product as per the final product specifications. In industrial glove manufacturing process, latex-based compound is prepared under two process steps as 1st stage compound preparation and 2nd stage (final) compound preparation. Compounding ingredients for 1st stage compound preparation process include: surfactants, cross linking agents, accelerators, activator, antioxidants, antiozone, waxes, anti-foam, anti-bacteria/ fungus, fillers, dispersing agents, waterproofing agents. Compounding ingredients for final compound preparation process included: 1st stage compound, pigments, thickening agents, bonding agents and smelling agents (Akabane, 2016; Rubber Research Institute of Sri Lanka, 2003).

3.2.3. Latex

The basic raw material used in producing the compound is centrifuged latex. Centrifuged latex is made by removing non-rubber part and concentrating natural latex which is tapping from Brasiliensis tree. In centrifuge latex making process raw latex which is harvest from field contain about 70% non-rubber and water, is concentrated and purified by centrifugation to a 60% rubber concentration and stabilized by adding lauric soap for long term storage (Rubber Research Institute, 2016; Rubber Research Institute of Sri Lanka, 2003).

Raw centrifuge latex quality is very critical and important in process controlling and product quality as it is the main component of the industrial glove. Accordingly, Viscosity, mechanical stability time (MST), total solid content (TSC), dry rubber content (DRC), Toluene swelling index (TSI), Alkalinity (Ammonia Content), KOH number and Volatile fatty acid number (VFA number) are measured during incoming quality inspection (Rubber Research Institute of Sri Lanka, 2003; Sin, et al., 2016; Yip & Cacioli, 2002).

3.2.4. Surfactants

Surfactants are added in to compound to lower the surface free energy of latex particles. Further, surfactants perform functions of dispersing agent, wetting agent, emulsifiers, stabilizers and foam promoters. Accordingly, surfactants are carrying important role of maintaining even properties in compound all over the process in order to have consistence in final product quality. Generally, potassium hydroxide as stabilizer/ pH controller, surfinol as wetting agent and potassium laurate as stabilizer are commonly used surfactants in natural rubber-based glove manufacturing industry (Singh & Hui Mei, 2013).

Potassium hydroxide- Used as a stabilizer as well as pH controller. Centrifuged latex pH values has to vary in between 9.5 to 10.5 to behave as stable colloidal suspension. Further, acidic nature of other compounding ingredients, early coagulation can be occurred during compound making process. Here potassium hydroxide surfactant is added to compound as a stabilizer as well as a pH controller to mitigate the issue (Aravind Mafatlal Group, 2010).

Surfynol- Used as a wetting agent and provides additional functionality such as high flow ability, high deformability, reduction of surface tension, etc. It contains mainly tetra-methyl-decynediol, gemini surfactant and other ingredients. Basically, it facilitates impregnation of fabrics or fibers with latex (Wong, et al., 2007).

Potassium laurate- is use as a stabilizer for enhancing the mechanical stability time in order to have long storage time without change of compound properties (Than, et al., 2018).

3.2.5. Cross Linking (Vulcanizing) Agent

Crosslinking is chemical process that transfer rubber particles in to crosslinked rubber structure, resulting much improved mechanical properties and stable rubber product. The crosslinking process is usually initiated with crosslinking agents, activators and accelerators under heating with polymers at temperature around 120 °C for 2 hours' time. Most common vulcanization agent in glove manufacturing industry is sulfur, in dispersion phase. Amount of Sulphur used in compound plays an important role in vulcanizing process as insufficient amount may lead to partially vulcanized structure, while excess sulfur causes blooming effect. (polymerdatabase.com, 2015; Yip & Cacioli, 2002)

3.2.6. Activators and Accelerators

Vulcanization of rubber with only sulfur is extremely slow process and take several hours to fully cure at elevated temperature. If polymers are exposed to high temperature in the presence of oxygen for a long time, degradation of polymers takes place and results in poor mechanical performance. Further it would not be economical to cure rubber with sulfur alone. Accordingly, activators and accelerators are added to the compound for effective vulcanization process.

Activators initiate the vulcanization reactions. Zinc oxide dispersion is the most common activator used in glove manufacturing process

Accelerators are used for speeding up the process of vulcanization and minimize the rubber exposure time for elevated temperature. Mostly used accelerator in industrial glove manufacturing industry are zinc diethyldithiocarbamate (ZDEC) (Ph 8.5-11, TSC 50%), and SETSIT (reddish brown liquid).

3.2.7. Antioxidants & Antiozonants

Natural rubber articles need protection against environmental degradation caused mainly by oxygen and ozone. Accordingly, antioxidants and antiozonants are added in order to minimize environmental exposure or decomposition from environmental conditions such as solvents, oils, detergents, heat, cold, light, ozone, and oxygen. In natural rubber based industrial glove manufacturing industry also mandatorily use antioxidants and antiozonants, in order to gain required durability and service period. Otherwise defects such as color fading, heat instability, cracking, and poor performance can occur with time (Tan, et al., 2018).

3.2.8. Waxes

Wax are made of paraffin material extracted from crude oil and other ingredients emulsifying. Mainly wax are added in industrial glove manufacturing as a processing aid for easy glove removing, to enhance storing ability, enhance ageing resistance, reduce electrical conductivity, enhance coating surface finishing & protection, etc. Accordingly, suitable waxes in glove manufacturing industry must have good mixing ability, even film making ability, good covering power, and nonstick characteristics (Rubber Research Institute of Sri Lanka, 2003).

3.2.9. Anti-foam

Anti-foam agents are used in natural rubber based industrial glove manufacturing for stopping foam formation or bursting available foams in compound, because foams causes pin halls, air bubbles or uneven thickness on glove coating. Further, this is used as a dewebbing agents to avoid membranes formation in-between finger crouches of a dipped former once the mould has been removed from compound on dipping process (EVONIC Industries, 2017).

3.2.10. Anti-bacteria/ fungus

Sanitized and actifresh are used to get rid of growing micro-organism, fungi and bacteria on rubber articles. Here those chemicals disrupt the metabolic process of growing, functioning and reproducing of microorganisms. In addition to that anti-bacterial and anti-fungal chemical must have characteristics such as durable protection, leach resistance, protection against microbial caused discoloration, rubber material protection, safe handling, etc. If particular product is sanitized treated and protected from micro-organism, fungi and bacteria, product can be tested at notified body and can claim for sanitized logo (Figure 3.2) marking as for the standard EU Regulation EU No. 528/2012 (BPR) (Chang, et al., 2018).

Figure 3.2-Sanitized Logo

3.2.11. Filler

In industrial glove manufacturing industry, mainly fillers used to increase the volume and for low cost production purposes. In addition to that, fillers offer other benefits such as increasing reinforcement, improving hardness and stiffness and facilitating processing of rubber. Even though all performance enhancements of rubber article are mainly dependent on filler material characteristics such as particle size, surface activity, persistent structure, porosity, etc. Further reinforcing ability of a filler is of much important in industrial glove manufacturing industry, since it generates inter molecular bonds in between fillers and rubber vulcanizate to improve the mechanical properties (RubberCare Protection Products Sdn Bhd, 2019; Rubber Research Institute of Sri Lanka, 2003).

The natural rubber coating in the sample gloves used for the project is containing non-reinforcing $CaCO_3$ as the filler. Here fillers are used to extend the physical properties usually to reduce compound cost, to increase the viscosity and to influence the chemical stability of the compound (RubberCare Protection Products Sdn Bhd, 2019).

3.2.12. Pigments

Both rubber and vulcanized rubber materials are subjected to heating processes, phase transition processes, mixing processes, deformation, degradation, and subjected to stresses while processing as well as in the applications. Therefore, selecting coloring ingredients and method are of very important in rubber glove manufacturing industry. The selected pigment shouldn't contain toxic or destabilizing substances which negatively effect on rubber product, product manufacturing process as well as product compliance related to hazardous materials. Other than that, properties of color pigments are also very important in glove manufacturing such as color consistency, and heat resistance to achieve expected final product quality (Yip & Cacioli, 2002).

In glove industry liquid color pigments are added to compound during mixing process to achieve required color. Accordingly pigments specifications such as color strength, pH, bleeding property, total solid content (TSC) are monitored while selecting the correct pigments (NG , et al., 1994).

3.2.13. Thickening agents

Thickening agents or thickeners are used to increase viscosity of latex compound without affecting other properties. Purpose of achieving or maintaining optimized viscosity in latex based compounds in glove industry is to achieve required coating thickness/ glove thickness and other glove properties. Methocel HPM 450DS, Acrysol, Paragum are some of the thickening agents used in industrial glove manufacturing industry (Kassam, et al., 2010).

3.2.14. Bonding agent

Bonding agents are used to improve bonding strength in between liner and coating. Mainly liners are made of polymeric material such as polyester fibers, nylon filaments, acrylic fibers, cotton fabrics, glass fibers, steel wires, polyethylene fibers, etc. Therefore, an incompatibility in between liner and natural rubber-based coating causes delamination, poor bonding strength and low abrasion resistance of industrial gloves. This can be minimized through adding some bonding agents to compound which improves inter bond strength in liner and coating through a slight penetration (Yip & Cacioli, 2002).

3.2.15. Smelling agent

The offensive odor of natural rubber-based product is a massive problem in commercial customer attraction. Mainly this unpleasant odor is generated due to microbial degradation of carbohydrates, proteins, and other non-rubber components of natural rubber latex while storing, processing, even in cured product. Therefore, smelling agents such as vanilla flavoring ingredients come to compound in natural rubber-based glove manufacturing industry in order to avoid that offensive odor. Generally Vanilla ingredients in liquid form used in industrial glove manufacturing industry while quality controlling through pH, total solid content and viscosity (Gulf Flavours and Food Ingredients FZCO, 2014).

3.2.16. Dispersing Agents

The chemical ingredients come in solid form or powder form and they are required to mill in ball mill or pebble mill in order to make dispersions. Generally compounding ingredients such as sulfur, zinc oxide, calcium carbonate, antioxidants come in powdery form, to convert them in to liquid form, the further reduction of particle size by milling is required to prepare dispersions. The purpose of making dispersion to have even slurry mixture is needed to ensure stable quality compound, but some ingredients tend to settle down with time. Dispersing agents are added to the compound to avoid this. The purpose of dispersing agents is to have even compound mixture through minimizing the settling of ingredients while processing. Most commonly used dispersion agent is Naphthalene condensate (Tamol) (Rohm and Haas, 2008). Further polyurethane dispersion (Impranil) (Covesto, 2019) fluorine compound (Nuva TTC) (Alahi, et al., 2018), titanium dioxide can also be used.

3.2.17. Waterproofing Agents

Waterproofing agents are used in industrial glove manufacturing industry to have water repellent properties and improve resistance to water absorbing in final glove. Mostly industrial glove applications such as food handling, material handling at wet condition require to have waterproofing properties. Accordingly, waterproofing agents such as waxes and other surface energy reducers are added to compound such as waxes and other surface energy reducers. Mostly used waterproofing agent is Nano water repellent (ANTIWET FH919/ organic silicone compound) as it reduces the surface energy drastically on coating surface. It boosts water repellency and creates a greater looking water beading appearance on the surface so that results in long lasting protection as well.

3.2.18. Coagulant solution

Coagulant solutions are used for coagulation of compound on the lined former. Generally, 2% calcium nitrate mixed methanol solution is used as coagulant solution in industrial glove manufacturing industry. Formers with liner firstly dipped in coagulant solution and let it dry prior to be dipped in compound. Methanol will be evaporated due to high volatile nature and Ca^{2+} irons will remain on the liner which will act as coagulant agent while dipping in natural rubber-based compound (Than, et al., 2018).

3.2.19. Swelling solution

Swelling agents are used to create crinkle texture on uncured glove in order to have required grip on natural latex based industrial gloves. Accordingly, uncured glove is dipped in swelling solution which is made by adding acetic acid up to 3.5% on xylene solvent (Packham, 2006).

The uncured glove which is made of dipping former with liner in compound, should be dried for some extent to have thin rubber layer of the coating prior to dip in swelling solution. Then glove is dipped in swelling solution, the dried top layer tends to expand over the coating cause crinkle pattern on the glove.

3.2.20. Calcium water

Calcium water solution is used for post coagulation dipping of uncured glove prior to curing process to avoid migration of non-rubber parts to glove surface and to have good gel strength. If uncured glove not dipped in post coagulation calcium water, coating trends to brake or fall down and non-rubber parts migrate to the surface and cause dirty mark defects, color variation defects, stain mark defects etc. Calcium water solution is made by mixing calcium nitrate on water up to a strength of 8% (Yip & Cacioli, 2002).

3.2.21. Leaching Water

After being dipped in compound, uncured green glove is passed through some online washing process called leaching. At this stage uncured green glove contain much of unreacted/ additional chemicals which should be removed prior to curing. So, gloves on formers are going through the water tank. This water tank called leaching tank and water in this tank need to be refreshed frequently to maintain adequate washing in order to have uncontaminated glove.

3.3.Manufacturing methods of Industrial Gloves

There are three main types of manufacturing methods of gloves, namely, direct dipping, coagulant dipping and heat sensitive dipping. Direct dipping is the simplest dipping method. The clean former is immersed in the compound for a specified time and withdrawn slowly. Then it is left for a given time for drying followed by vulcanizing. However, the thickness of the glove can be improved by immersing again after drying partially. The thickness of this glove is mainly dependent on the Total Solid Content (TSC) and the viscosity of the latex compound (Akabane, 2016).

Coagulant dipping is a complex process than the direct dipping. The clean former is firstly dipped in the coagulant solution and then it is dipped in the compound. In between two dipping instances and after dipping in the compound, there is a specific time that is given to be dried. As in direct dipping, the thickness of the rubber layer can be increased by immersing the former again in the coagulant and in the compound with partial drying. In here also, the final step will be vulcanizing. The coagualant used in this process is usually calcium salts. Calcium nitrate or calcium chloride are the main materials that are used. The coagulant solution is prepared mainly with water or alcohol or a mixture of both (Akabane, 2016).

Heat sensitive dipping is heating the former to a temperature of 30 ^{0}C to 60^{0}C before dipping in the compound (Akabane, 2016). After leaving the former dipped in the compound for a given time, the former is slowly withdrawn from the compound and vulcanized. But however, this method cannot be used for industrial glove manufacturing because when industrial gloves are manufactured, a liner is loaded to the former before dipping in the compound. The liner cannot be heated as it destroys the liner properties (Akabane, 2016).

3.3.1. Compounding

Under compounding section, operations such as dispersion making, ball milling, pebble milling, mixing, compound making, compound maturation, sample dipping and testing will be carried out. Here dispersions of 1st stage compounds, 2nd stage compounds, coagulant solutions, solvent solutions and calcium water solutions are produced for dipping operations.

In quality controlling, cloud test for dispersions, toluene swelling index, mechanical stability time and pH for 1st stage compounds are determined. 2nd stage compounds are used for test sample dipping and pH and specific gravity of other solutions are monitored (Rubber Research Institute of Sri Lanka, 2003).

3.3.2. Glove mass production

Glove mass production process is carried out with automated production lines which is capable of dipping, leaching and curing in order to produce supported gloves. Accordingly, manual handling is required only for liner loading to plant, gloves unloading and other process controlling purposes during the production runs. (RubberCare Protection Products Sdn Bhd, 2019).

In production operation, firstly liners load in to metal former and dress as required, secondly dipped in coagulation solution (if the coagulant dipping method is used), let it drain for excess and let dry in atmospheric temperature, thirdly dipped in compound, let it drain for excess and let dry in atmospheric temperature, fourthly dipped in swelling solution to have crinkle pattern, fifthly dipped in calcium water solution to have required gel strength, sixthly going through the leaching tank to get rid of excess chemicals in uncured glove, seventhly do semi curing in order to remove water part from glove prior to curing, finally going through oven at the range of 80 ^{0}C and 120 ^{0}C in order to cure the glove (NG , et al., 1994).

3.4.Abrasion performance of Industrial Gloves

Industrial gloves are designed for different applications based on the customer requirement. Among those applications, mechanical resistance gloves, cut resistance gloves, impact resistance gloves, heat resistance gloves, fire resistance gloves, chemical resistance gloves, electrical shock resistance, arc flash resistance gloves, welding protection gloves, bacterial and microorganism resistance gloves, anti-statistic gloves, virus resistance gloves, food handling gloves, oil resistance gloves, etc can be seen. Accordingly, glove testing standards have been developed in order to verify, demarcate, and standardize product safety compliance for the application. Refer Appendix 1.

Under glove standard EN388:2016- Mechanical performance, abrasion resistance, cut resistance, tear resistance, puncture resistance and impact resistance are measured on general purpose industrial gloves. Predicted performance of glove is evaluating in number of ways. One of the most commonly referred method is abrasion resistance in Martindale abrasion tester. On the whole, abrasion resistance performance may contribute to the overall evaluation of glove performance in the aspect of durability, level of safety and ability to retain appearance (Adamiak, 2012; Peash, 2015; Textor, et al., 2019).

3.4.1. Abrasion resistance

Abrasion is process of surface wearing or scraping off material as a result of flat rubbing contact with another material. Quantitatively this can be defined as the weight loss or thickness reduction due to frictional force. Hence abrasion resistance is the ability of material or structure to withstand in shear forces (Association for contract textiles, 2011). In industrial application, glove can be abraded in many ways such as edge abrasion, flat abrasion, and other type of wear etc. In addition to that abrasion resistance of glove depend on material, temperate, humidity, pressure applied on object, moving rate, texture and nature of surface which rub against. In consequence analyzing of abrasion resistance performance of gloves in quantitative manner have limitations. Martindale test method is limited to measure flat abrasion resistance while keeping all other causes of abrasion constantly (Ertekine, 2017; Özdil, et al., 2012).

3.5.Factors effecting on abrasion performance of industrial gloves

There are many factors affecting on the final abrasion performance of the industrial gloves with respect to the glove composition and processes which are carrying out for processing industrial gloves and testing of abrasion performance. Consequently, main concerns with respect to abrasion performance of industrial glove can be converge to pre-coagulation concentration, filler characteristic and amount of curing/ crosslinking density (Rubber Research Institute of Sri Lanka, 2003).

3.5.1. Coagulant percentage on pre-coagulant dipping

As explain in glove manufacturing process, liner on metal former is dipped in pre-coagulant solvent which is made of calcium nitrate mixed methanol solution in order to incorporate coagulating agent on the liner. The coagulant percentage on liner basically control the compound layer which is built on second dip in compound tank.

If liner contamination percentage of coagulant is not adequate, there is tendency of compound to go through the liner pores causing penetration defect. Where compound coating passes through the liner and make rubber layer inside the shell which feel rubber on hand when glove is worn. Generally natural rubber latex cause skin allergies due to contamination with proteins as well as uncomfortable nature, those penetrated products categorized as defects (Walsh, et al., 2003).

In case coagulation percentage is too high, rubber particles tend to coagulate on the top of the liner that causes delamination defect. In case of compound layer forms on the top of the shell without any penetration, poor bonding occurs as well as layer separation. Further this poor bonding as well as layer separation are of high concerns when considering abrasion performance of industrial glove manufacturing process.

By considering above factors affecting abrasion performance of the industrial gloves, it is required to have system for close monitoring of coagulation percentage of coagulation solvent, coagulation dipping time, draining time, soaking time in order to maintain even coagulation density of the liner prior to dip in compound tank as well as to maintain even abrasion performance (RubberCare Protection Products Sdn Bhd, 2019).

3.5.2. Filler type and characteristics

Second main concern is with respect to abrasion performance of the industrial glove is compound recipe. Generally natural rubber-based compound recipe basically contains latex, curing pack, fillers, pigments, processing agents and other ingredients which added for control of degradation and other negative effects. Here filler material plays vital role in achieving abrasion performance of the industrial glove as well as optimizing of manufacturing cost.

Basically, filler materials which are added to liquid based compound cause mainly two impacts as improving reinforcing effect on rubber and increasing the volume of rubber for low cost production. Other than that, they improve hardness of rubber, improve stiffness of rubber, facilitate processing of rubber and enhance age resistance properties. Nevertheless, filler characteristics are highly influencing above highlighted effects on rubber products such as specific gravity, hardness, particle size (determines surface area per gram), particle size distribution, shape of particles, aspect ratio (the ratio of length to diameter), surface activity (physio-chemical nature), persistent structure, porosity, surface chemistry etc.

Specific gravity of polymer materials varies from 0.9 to 1.4 whereas for filler material 2.3 to 2.8. Thus, incorporating fillers on polymer composite increases specific gravity considerably. Hardness of filler materials is also importance for final hardness property of the composite. Generally hard filler materials such as crystalline silica used for applications where high abrasion resistance required, but processability is difficult due to machine wear and degradation of fiber length in complex composites. Soft fillers have high ability of absorbing stress and maintain required softness of the composite. Particle size, particle size distribution, shape, aspect ratio, aggregates and agglomeration are filler characteristics depend on physical shape and nature. Those characteristics influence effective surface area, filler to polymer strength of interactions, composite morphology, and final product performance. Abrasion resistance of composite is improved with effective surface area and filler to polymer interactions.

In commercial production, calcium carbonate, treated calcium carbonate, carbon black, silica, clay, talc powders are used as filler material in rubber product manufacturing industry. Mostly calcium carbonate and treated calcium carbonate are used as non-reinforcing fillers in liquid rubber-based product manufacturing industry.

3.5.3. Curing percentage/ Crosslinking density

Curing percentage and crosslinking density is one of the most critical parameters for the abrasion performance of the product. Basically, these parameters decide the strength of rubber article and resistance to erosion caused by scraping, rubbing and other type of mechanical wear and tear off of material from the article. This allows article to retain its shape/ integrity and deliver its maximum efficiency in the relevant function.

General un-vulcanized rubber is normally in weak and deformed against stress. Accordingly, un-vulcanized rubber in solid form or liquid form are used in shaping process in order to form desired shape. Latter vulcanization reaction leads to the formation of inter-molecular bonding among the unsaturated rubber molecules with three-dimensional network. Due to this structural modification rubber article's mechanical properties such as tensile strength, hardness, stiffness, and abrasion resistance are enhanced. In spite of friction coefficient, permanent set, and hysteresis like parameters are decreasing with the increase of crosslinking density.

The common vulcanizing agent in natural rubber-based glove manufacturing industry is elemental sulfur or sulfur donner material in powder form or slurry. Consequently, non-sulfur vulcanizing agents such as metal oxide or peroxides are also used.

3.6.Filler characteristics effecting on abrasion performance of latex gloves

Basically, there are two different types of fillers based on chemical nature and microstructure with respect to interactions with polymer chains. Namely reinforcing fillers and dispersion fillers. Mineral fillers with lyophilic or lyophobic surface character, which is imparted by surface chemical active nature and ability of creating interactions in between colloidal and the liquid cause for the final product performance. Here chemically surface active functional groups on filler materials such as phenolic (OH), carboxylic, (CO-, COOH), sulfur, metal ions, ketones and lactones, etc (intensity factor) are responsible for interacting with the rubber. If filler characteristic is lyophilic, inter molecular attractions are built in between filler materials and polymer chains. This is the cause for high mixing ability, strong stable solution, thermodynamical stability, and high uniformity of the compound/ final product (Veselovsky & Kestelman, 2002). On the other hand, fillers in lyophobic nature which has no inter molecular attraction forces or repelling forces in between fillers and polymer chains is the cause for settling of filler materials, material/ layer separation or filler materials trapping in polymer chains while the curing lead for inhomogeneous compound or product performance. In both scenarios it is required to create polymeric composite material with tremendous reinforcing structure resulting in improvement of the physical-mechanical properties of the composite material. Further some filler material surface modified to have required bonding and material structure in order to enhance product performances (Rothon, 2000).

Generally, parallel to increase the filler material percentage in a compound, performance such as strength, stiffness and abrasion resistance are increased up to some critical point, after that it starts to decline with filler percentage due to micro cavitation and de-bonding takes place. If the filler percentages are below the critical point, it causes reduced internal stress in the structure due to inter molecular attraction forces leading to properties enhancement, but going beyond the critical point of filler packing density, it buildup internal stress, restrict polymer mobility and performance will be declined (Khanal & Morrison, 2012).

Surface energy and surface tension in between filler material and polymer are also very critical factors when it comes to natural rubber based composite polymer materials. Surface active nature, ability of making bonding, active groups and intention of making bonds and absorbing free radicals are the main factors that decide the surface energy of a material. High surface energy nature helps to create good interactions and bonding between filler material and other materials in composite in order to have required performances such as strength and abrasion resistance. Further, high surface energy related to high surface tension shows low contact angle of filler material and polymeric matrix that is conditions for larger contact area and causes efficient bonding in between the materials. However, most of polymeric materials are having low surface energy and poor wetting properties leading to poor interactions between filler materials and polymer materials. Therefore, use of various techniques such as corona or flame treatment in air, or oxygen or nitrogen plasma treatment in a vacuum will increase the surface energy of polymer that in turn will improve wetting of polymer with filler leading to formation of developed interfacial area and good bonding. (Abdullah, et al., 2013).

Particle size, surface area and particle size distribution of filler material is affecting on abrasion performance of the latex glove. Correct particle size and distribution of filler material create grater surface area and better filler- rubber interfacial adhesion resulting in an improved abrasion resistance and packing density. In liquid based compound in dip product manufacturing, fineness of filler material increases interface between filler and latex matrix providing a better abrasion resistance than coarse filler and latex composite (Zhang, et al., 2010).

Filler rigidity and persistent structure are also critical parameters in polymer composite material in order to achieve required performances. Rigid filler material-based polymer composite shows better abrasion resistances performance but tend to wear off of processing machineries. On the other hand, soft filler filled polymer material shows poor strength and fracturing with stress. The persistence structures of filler materials inside of polymer such as primary particles, aggregation and agglomeration are influencing finished product performance based on molecular structure and bonding density. Individual primary particles in the structure shows better performance than aggregation and agglomeration due to better contact and high ability of adhesion with polymer material. In aggregation structure filler material particles bond with each other with some weak diffusion bond in nature (Sun, et al., 2018). Here aggregation structure can be segregated in to two groups based on degree of aggregation as low structure-30 particles/aggregate and high structure-200 particle/aggregate. Agglomeration which are called secondary aggregation with very weak bonds of aggregates due to Van der Waals bonds. Anyway aggregates and agglomerates in the polymer composite structure leads to poor performance than individual particles (Arayapranee, 2012; Wang, et al., 2010).

3.7. Silica filler characteristics effecting on abrasion performance of latex gloves

Crystalline Silica is the most abundant mineral in the world, being found as the component in the other minerals and mostly as sand. Few silica based mineral types used in polymer industry as filler materials such as quartz, novacite and crystobalite. Quartz have required composite performance of high hardness, chemical inertness, heat resistance, low coefficient of thermal expansion and good electrical insulation properties, etc. Generally crystalline silica is used as semi reinforcement filler material in rubber industry as well as reinforcement filler material with silane coupling agent, but due to toxicity concerns of crystalline silica, its usefulness is limited.

Further, synthetic silica materials are manufacturing based on industrial requirement and advanced morphological characteristics such as precipitated silica and fumed (pyrolytic) silica. Precipitate silica is an amorphous form powdered silica material which is made through the chemical reaction in Figure 3.3 from a solution containing silicate salts (Pasbakhsh, et al., 2009).

$$Na_2(SiO_2)_7 + H_2SO_4 + O \rightarrow 7\ SiO_2 + Na_2SO_4 + H_2O$$

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$$

Figure 3.3-Chemical reaction for preparation of Precipitate Silica

Precipitate silica is the most commercially consuming silica material for industrial purposes and it shows porous structural nature. Here primary particle size differs in 5 to 100 nm range and agglomerates in 1 to 40 µm. (specific surface area 5-100 m2/g, Density: 1.9 - 2.1 g/cm3). Fume silica (pyrogenic silica) is made through the chemical reaction in a flame as per Figure 3.4 in between silicon tetrachloride and water vapor. Here microscopic porous droplets of amorphous silica are produced, fused into branched structure and agglomerate into tertiary particles. Therefore, fume silica is very light powder with high surface area and water absorbing characteristics. Primary particle size is 5–50 nm. The particles are non-porous and have a surface area of 50–600 m2/g. The density is 160–190 kg/m3. Fumed silica normally classified into two classes as treated and untreated (also known as hydrophilic and hydrophobic) based on commercial requirement. Further due to this three-dimensional structural nature and liquid absorbing ability, fumed silica is used as thickener and reinforcing filler in many industries (Rueby, 2019).

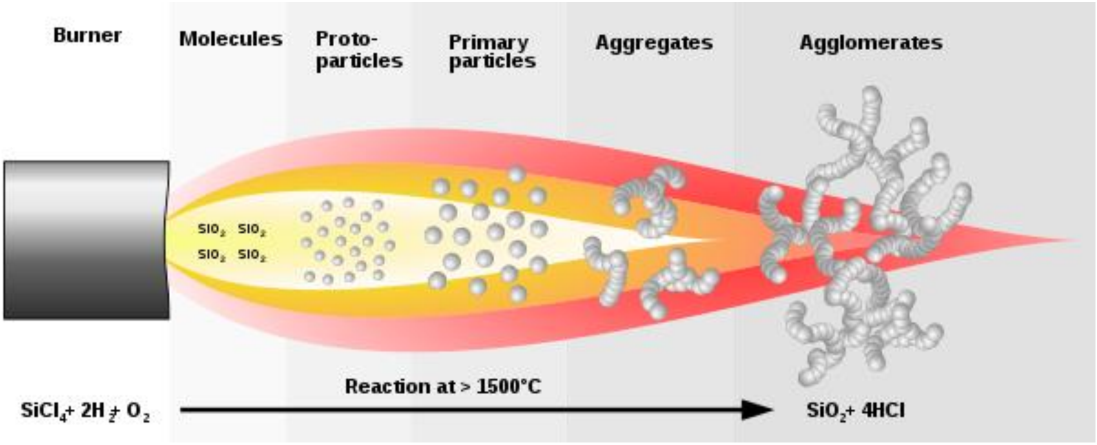


Figure 3.4-Fume silica making process

Silica is used as filler material in dry rubber industry as well as in liquid rubber-based industry as substitute material for carbon black (most common reinforcement filler material). Mostly silica materials are more expensive than carbon black, but performance are similar or beyond as carbon black. Basically, silica materials are used for improvement of tear strength, to control of heat buildup, improvement of abrasion resistance, white color and increase in adhesion properties of multi-layer products such as tires. Silica filler material characteristics are varying with its physical properties such as particle size, structure as well as chemical properties such as extent of hydration, pH, and composition. Physical properties of silica material depend on the way of silicon and oxygen are arranged in a tetrahedral structure of a 3-D lattice and amorphous structure based on short range crystals in random arrangement. Chemical Properties of Silica can be extended with surface silanol concentration (silanol groups —Si—O—H) influence the degree of surface hydration, surface acidity which is controlled by hydroxyl groups on the surface and is intermediate between rubber–filler interaction (EVONIC Industries, 2011).

Using of silicon filler material causes some limitations in manufacturing process as well as polymer-based products such as gloves, tires, coated fabrics, garments, etc. Basically, increase of viscosity during compounding, deactivation of accelerator system and machine wear off can be considered as processes limitations and harmfulness can be considered as product limitation.

3.8.Silane coupling agent

Silane coupling agents are used when the silica is used as a filler material in compounding, as a linking agent of silica and polymer material. Silane coupling agent is a chemical made of silicon-based chemical which is containing two type of reactive ends as inorganic and organic in the same molecule. General structure of silane coupling agent can be represented by chemical structure $(RO)_3SiCH_2CH_2CH_2\text{-}X$, where RO is a hydrolysable group, such as ethoxy, methoxy, or acetoxy, and X is an organofunctional group, such as epoxy, amino, methacryloxy, etc (Krayden INC, 2009).

According to the chemical structure and characteristics of Silane the coupling agent, it can act as a joining material of an inorganic substrate such as metal, glass or mineral and an organic material such as an organic polymer, adhesive or coating like dissimilar materials. Generally, polymers are reinforced with fibers or mineral materials in order to improve product performance, whereas Silane coupling agent is involved in interface or interphase region, in between polymer particles and inorganic substrate to create bonding and links. The ability of generating inter-molecular bonds, adhesion lead to creating of strong polymer composite materials with improved physical strength, abrasion resistance, coefficient of expansion, concentration gradients and retention of product properties. Further Silane coupling agent is used as the solution to avoid mixing difficulty of rubber with pure silicas, as the polarity-difference between silica and rubber results in incompatibility. Here silane coupling agents acts as a bridge to overcome polarity difference and poor mixing. In addition to that adding silane coupling agent to polymer-based compound gives many advantages such as better wetting of inorganic substrates, smoother surfaces of composites, lower viscosities during compounding, less catalyst inhibition of thermoset composites, clearer reinforced plastics, etc (Xie, et al., 2010).

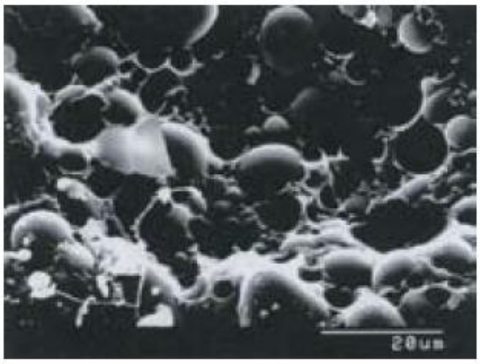


Figure 3.5-SEM image- Silica-filled epoxy resin without silane coupling agent

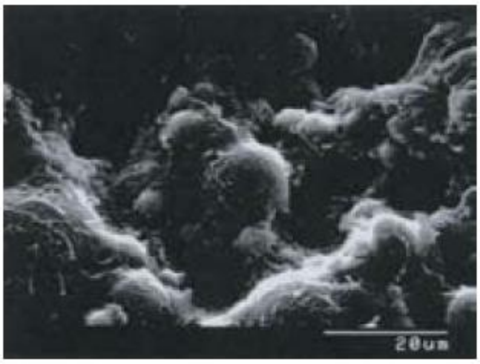


Figure 3.6-SEM image- Silica-filled epoxy resin with silane coupling agent

Figure 3.5 and Figure 3.6 describe the scanning electron microscope image of silica filled natural rubber-based compound shows difference in adhesion between a silica filled compound with silane coupling agent and without silane coupling agent. The compound structure with silane coupling agent shows bonded silica particles apparently, whereas compound without silane coupling agent shows clean silica particles due to poor inter material interactions and weak structure.

The chemical reaction in Silane bonding to the inorganic substrate can be described as in Figure 3.7. Generally, silane coupling agent contains three reactive groups basically methoxy, ethoxy or acetoxy groups which have ability to bond with hydroxyl groups on inorganic substrates like silicon, aluminum and other heavy metal structures. In silica filler material filled compound, alkoxy groups on silicon are hydrolyzed with silanols and create oxane bonds on the silicon filler material by eliminating water.

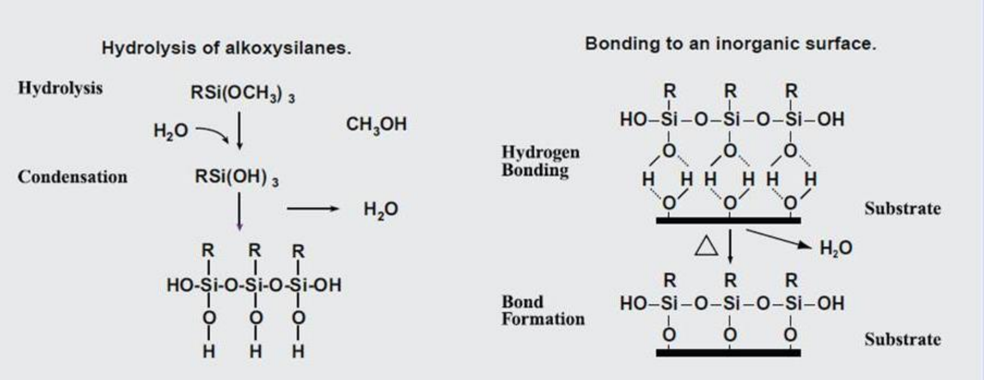


Figure 3.7-Silane Bond with inorganic substrate

The bond in between polymer material and silane coupling agent depends on reactivity compatibility of polymer material to silane coupling agent. Therefore, selection of type of silane coupling agent depends on the type of polymer as well as reactivity. Generally, epoxysilane or amino-silane can be used for epoxy resins, amino-silane used in phenolic resin, methacrylate silane used for styrene and unsaturated polyester resins. Further polymer material and silane coupling agent bond can be described through the inter-diffusion and inter-penetrating network formation in the polymer and inorganic material interface as Figure 3.8.

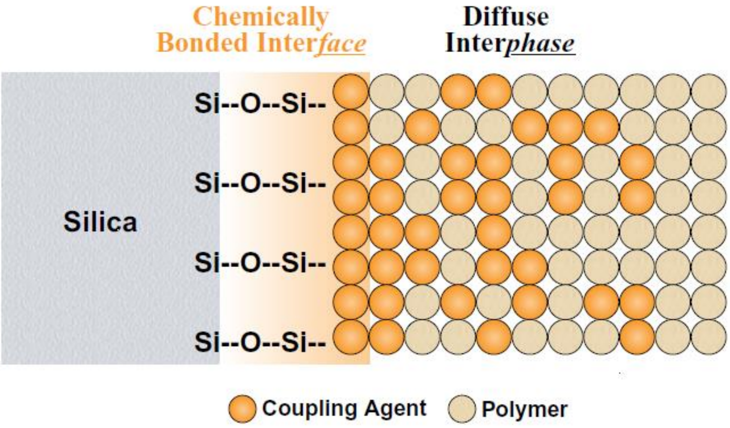


Figure 3.8-Silane bond with organic substrate

When selecting a suitable silane coupling agent for polymer composite material, the material compatibility, chemical characteristics, solubility characteristics, structural characteristics and thermal stability should be considered in order to have enhanced physical properties of composite. Most of the silane coupling agents containing organofunctional alkoxysilane groups and organic groups as in Figure 3.9 and shows different reactivity nature. According to the reactivity of organic group, silane coupling agents can be categorized as Table 3.2 (Mittal, 2004).

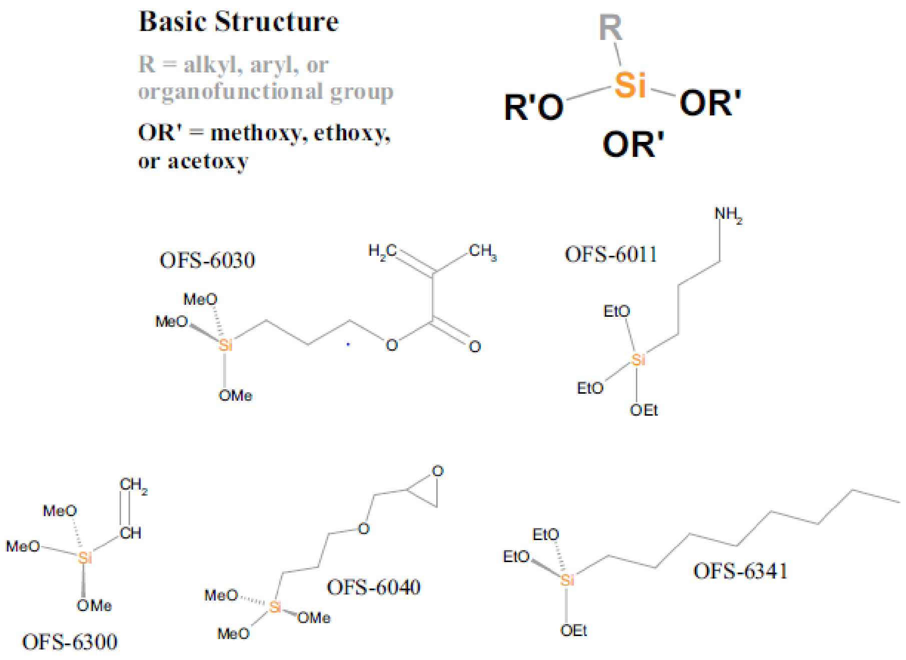


Figure 3.9-Silane coupling agent variations – basic structures

Table 3.2-Characteristics of Various Organic Substituents on Silanes

Organic Substituent	Characteristics on Silane
Methyl group	Hydrophobic, Organophilic
Phenyl group	Hydrophobic, Organophilic, Thermal Stable
Isobutyl group	Hydrophobic, Organophilic
Octyl group	Hydrophobic, Organophilic
$-NH(CH_2)_3NH_2$ group	Hydrophilic, Organoreactive
Epoxy group	Hydrophilic, Organoreactive
Methacryl group	Hydrophobic, Organoreactive

Selecting of suitable silane coupling agent type for polymer compounding application are required to have desired finished product properties. Table 3.3 gives silane coupling agent recommendations for various polymers based on organoreactive characteristics of polymer groups in silane.

Table 3.3-Silane Coupling Agent Recommendations for Various Polymers – Matching Organoreactivity to Polymer Type

Organic Reactivity	Application/ Suitable polymers
Amino	Acrylic, Nylon, Epoxy, Phenolics, PVC, Urethanes, Melamines, Nitrile Rubber
Benzylamino	Epoxies for PCBs, Polyolefins, All Polymer Types
Chloropropyl	Urethanes, Epoxy, Nylon, Phenolics, Polyolefins
Disulfido	Organic Rubber
Epoxy	Epoxy, PBT, Urethanes, Acrylics, Polysulfides
Epoxy/Melamine	Epoxy, Urethane, Phenolic, PEEK, Polyester
Mercapto	Organic Rubber
Methacrylate	Unsaturated Polyesters, Acrylics, EVA, Polyolefin
Tetrasulfido	Organic Rubber
Ureido	Asphaltic Binders, Nylon, Phenolics; Urethane
Vinyl	Graft to Polyethylene for Moisture Crosslinking, EPDM Rubber, SBR, Polyolefin
Vinyl-benzyl-amino	Epoxies for PCBs, Polyolefins, All Polymer Types

However, recent researches have been conducted on improving the abrasion resistance properties using silica materials as the reinforcing filler for elastomer compounds (Hewitt, 2007). Abrasion resistance have been increased in tire industry, using silica with the coupling agent Silane (Ultrasil, 2017). In tire industry, using precipitated silica is one of the newest technologies to improve the rolling and abrasion resistance. But silica is a hydrophilic substance and it usually do not mix well with rubber which is hydrophobic. To chemically bind these two materials, a coupling agent, Silane should be added (EVONIK team, 2019).

Research are conducted on nano-sized silica particles modified with trialcxysilane to use as a filler material to improve scratch and abrasion resistance in coatings of transparent UV/EB curable acrylates which are used for polymer reinforcement (Bauer, et al., 2002). Further, recent studies on improving abrasion resistance in tire treads shows that silica filler material combined with silane can give synergistic effects (Sattayanurak, et al., 2019).

According to European Coatings Journal, it says silica coupled with silane, give a huge improvement in abrasion and tear resistance for polymers though they are very tiny particles (Roscher, 2003).

3.9.Literature review summary

There are many materials that are used in the glove manufacturing process. First stage compounding will be done with ingredients such as surfactants, crosslinking agents, accelerators, activators, antioxidants and antiozne, waxes, anti-foams, anti-bacteria, filler, dispensing agents and waterproofing agents. Second stage compounding will be done to the first stage compound using ingredients such as pigments, thickening agents, bonding agents and smelling agents. Other than these ingredients, other processing agents such as coagulant agent, swelling agent, leaching water and calcium water is also used.

The basic raw material for processing of compound is centrifuged latex. Natural latex which has 70% of non-rubber and water will be purified by centrifugation up to 60% of rubber concentration and stabilized by adding lauric soap. Surfactants creates lower surface free energy of latex particles as well as it is important as dispersing agent, wetting agent, emulsifiers, stabilizers and foam promoters. KOH is used as a stabilizer as well as pH controller. Surfinol is used as wetting agent and potassium laurate as the stabilizer.

Most common vulcanizing agent in glove manufacturing industry is sulfur dispersion. Zinc oxide dispersion is the most common activator. Zinc diethyldithiocarbamate (ZDEC) accelerator is used to speed up the process. Further, antioxidants and antioznants are also used against the environmental degradation.

When considering the manufacturing process of gloves, prior to commercial process, glove sample should receive the approval for finalized specifications. It is followed by raw material procurement and incoming quality controlling.

Automated production line will conduct the dipping, leaching and curing for supported gloves. Production process can be specified respectively as liners loading in to formers, dip in coagulation solution, drain, dry, dip in compound, dip in swelling solution, dip in calcium water solution, send to the leaching tank, semi curing and finally oven curing. Cured gloves will be inspected in the quality inspection where then it is packed and dispatched.

Abrasion is process of surface wearing or scraping off of material as a result of flat rubbing contact with another material. With the new regulations of the glove manufacturing, EN388:2016, under mechanical protection, Abrasion resistance is considered as a property that should be adhered. Mostly used method of evaluation of abrasion resistance is using Martindale abrasion tester. Martindale test method describe; circular specimen of glove material is abraded under constant pressure with lissajous cyclic motion on planner until breakthrough to occur. Abrasion contribute to the overall performance, level of safety and the appearance of the glove.

Main concerns with respect to abrasion performance of industrial glove can be converge in to pre-coagulation concentration, filler type/ characteristics and amount of curing/ crosslinking density.

Filler characteristics are also very important for abrasion resistance. Polymeric campsite material with a high reinforcing structure, will improve the performance of the glove. Further, amount of filler material is very important for abrasion as after and below a critical point defined for each filler material, abrasion resistance will decline due to cavitation and de-bonding. Going beyond the critical point of filler packing density cause for buildup of internal stress, restrictions for polymer mobility and performance declining.

Surface energy of filler material, particle size, filler rigidity and persistent structure are the other important characteristics in the filler material which affects the abrasion.

Generally crystalline silica used as semi reinforcement filler material in rubber industry as well as reinforcement filler material with silane coupling agent, but due to toxicity concerns of crystalline silica cause to limit of their usefulness.

Due to three-dimensional structural nature and liquid absorbing ability, fumed silica are used as thickener and reinforcing filler (substitute for Carbon Black) in many industries than crystalline silica or precipitate silica. However, increase of viscosity during compounding, deactivation of accelerator system and machine wear off and harmfulness can be considered as product limitation.

Silane coupling agent is a chemical made of silicon-based chemical which is containing two type of reactive ends as inorganic and organic in the same molecule. Silane coupling agents act as bridge to overcome polarity difference and poor mixing, better wetting of inorganic substrates, smoother surfaces of composites, lower viscosities during compounding, less catalyst inhibition of thermoset composites, and clearer reinforced plastics.

When selecting suitable reinforcing material and coupling agent for polymer composite material, the material compatibility and matching of chemical characteristics, solubility characteristics, structural characteristics and thermal stability in order to have enhanced physical properties of the composite and finished product should be considered.

However, to improve the abrasion resistance, silica and silane coupling agent are mentioned in number of studies and used in different industries. Specially in tire industry and coating industry. But information related to study of abrasion resistance of gloves is extremely limited and hard to find a study that indicated the use of silica and silane together to improve abrasion resistance of industrial gloves..

4. PREPARATION OF SAMPLES

4.1.Materials

Following materials were used in this experiment for preparation of dispersions, solutions, compounds and dipped glove samples.

Low ammonia centrifuged latex
Calcium carbonate
Precipitated silica powder (silica 20 – 200 microns)
Fumed silica powder (Aerosil 5-50 microns)
Silane coupling agent (si69)
Sulfur dispersion (Vulcanizing agent)
Zinc Oxide dispersion (Accelerator)
Dispersing agent
Thickener
Color pigment
Calcium nitrate (purity 99%)
Methanol
Acetic acid (purity 99%)
Xylene

4.1.1. Low ammonia centrifuged latex

Low ammonia treated centrifuged natural rubber latex was used as base compound material in this experiment. This was supplied by Glenross (pvt) Ltd and sourcing from rubber plantations located in Kaluthara area. Material characteristics were measured as, total solid content (TSC) in the range of 62±1%, dry rubber content (DRC) in the range of 60±1%, mechanical stability time (MST) less than 500s, volatile fatty acid (VFA) less than 0.02, alkalinity less than 0.03, and KOH number 0.5. Laboratory test report is given in the Appendix 2

4.1.2. Calcium Carbonate

Calcium carbonate slurry was supplied from Lanka minerals & chemicals (Pvt) Ltd and was used for the compound preparation. This was Ultra fine Calcium Carbonate comprising a concentrated dispersion with ground Calcite from Sri Lanka. The grade of the calcium carbonate used was DISPER C 75 3. Dispersion characteristics was measured for TSC was in the range of 72-75%. MSDS is given in the Appendix 3.

4.1.3. Precipitated silica

Precipitated silica was used as a semi-reinforcing filler in this experiment to replace some percentage of calcium carbonate non-reinforcing filler material. Precipitated silica was supplied by EVONIK (pvt) Ltd China. This material was characterized as 20 to 200 mμ in particle size. Precipitated silica contained physically bonded water around 5.35% and chemically bonded water around 2.3%. Specific surface area was in the range of 5-100 m2/g, agglomerate size was in the range of 1 - 40 µm with average pore size above 30 nm, density was in the range of 1.9 - 2.1 g/cm^3. Preciptated silica used in the experiement is shown in the Figure 4.1. MSDS is given in the Appendix 4.

Figure 4.1-Precipitated Silica

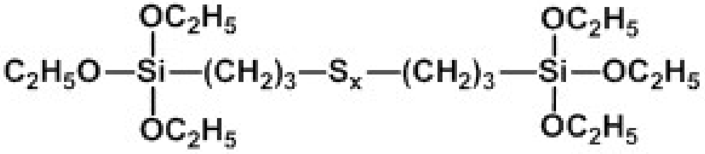
4.1.4. Fumed silica

Fumed silica is an extremely small powder particles with very low bulk density, high purity and volatile characteristics which was supplied from EVONIK (pvt) Ltd China. Primary particle size of fumed silica used for the experiment was in the range of 5–50 mμ and the surface area was in the range of 50–600 m^2/g. Density of the fumed silica was in the range of 160–190 kg/m^3. Fumed silica used in the experiment is shown in the Figure 4.2. MSDS is given in the Appendix 5.

Figure 4.2-Fumed silica

4.1.5. Silane coupling agent

Silane coupling agent is a pale-yellow thick liquid and used as combination material for organic and inorganic material. Silane coupling agent, Si 69 which was used in the experiment, was bought from Glovechem (pvt) Ltd in Pettah, Sri Lanka which was imported from EVONIK (pvt) Ltd. This has a sulfur content of 22.5%. The structure of the Silane coupling agent that was used is shown in the Figure 4.3. Silane coupling used in the experiment is shown in the Figure 4.4. MSDS is given in the Appendix 6.



$$C_2H_5O-\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}-(CH_2)_3-S_x-(CH_2)_3-\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}-OC_2H_5$$

Figure 4.3- Silane structure-Bis(triethoxysilylpropyl)tetrasulfide

Figure 4.4-Silane Coupling agent

4.1.6. Sulfur Dispersion

Sulfur dispersion which was used in this experiment was brought from Aquaspersions (pvt) Ltd, England. Dispersion material was characterized as pH in the range of 9.8-11.5, total solid content (TSC) in the range of 60-62%, and light yellow in color. MSDS is given in the Appendix 7

4.1.7. Zinc Oxide Dispersion

Zinc Oxide dispersion which was used in this experiment was brought from HANIL CHEMICAL IND.CO, LTD. Dispersion material was characterized as pH in the range of 8.5-11, specific gravity in the range of 5 to 6, and color in pure white. MSDS is given in the Appendix 8

4.1.8. Dispersing Agent

Potassium hydroxide, Potassium laurate (stabilizer), ethoxylate (Surfynol), Nonylphenol Ethoxylate (N40), Naphthalene (Tamol), and Bentonite clay were used as dispersion agent and bought from Glove Chem (Pvt) Ltd, Sri Lanka.

4.1.9. Thickener

Acrosole- WS(30) 140 was used as thickening agent in the experiment. Purpose of thickening agent was viscosity adjusting of the compound and coating thickness control through the compound viscosity.

4.1.10. Color pigment

In this experiment few color pigments were used for glove manufacturing process. Viscofil orange, Microtint 4154 orange, Microtint 4026 blue, Kramacryl FDA 4821 blue, Kramacryl 4749 green were bought from Haycolours (Pvt) ltd, Sri Lanka.

4.1.11. Calcium nitrate (purity 99%)

In this experiment 99% pure calcium nitrate crystals were bought from Devi Trading (Pvt) ltd in Pettah, Sri Lanka. It was used as coagulation agent in natural rubber dipping process. Density of the material was 2.50 g/cm^3.

4.1.12. Methanol

In this experiment methanol was used as coagulant media of the coagulation agent. Methanol was bought from CKG Chemicals (pvt) ltd, Malaysia. Specific gravity of the methanol was in the range of 0.8 to 0.7 units.

4.1.13. Acetic acid (purity 99%)

99% pure acetic acid was used in the experiment as texturing agent in crinkle texture creation process. Acetic acid was bought from Devi trading (Pvt) ltd, in Pettah, Sri Lanka. Here material was characterized as a specific gravity in the range of 1.0 to 1.1 units.

4.1.14. Xylene

In this experiment Xylene was used as solvent solution media for the crinkle texture creation process. Xylene was bought from Petrochemicals Malaysia Sdn Bhd, Malaysia. Specific gravity of the Xylene was in the range of 0.8 to 0.9 units.

4.2.Preparation of Dispersions

Generally, solid or powder materials are not added to liquid based compounds directly due to mixing difficulties as well as inhomogeneous characteristics. Therefore, those solid materials are converted to water-based dispersions with the help of milling machine or mixing machine prior to adding in to compound. Since precipitate silica and fume silica are small scale filler materials, pebble mill and magnetic stir mixing machine was used to mix precipitate silica and fume silica filler materials respectively. Dispersion materials were used to gain stability of dispersion and higher mixing tendency (otherwise silica materials are floating on top of water surface or tend to settle in the bottom).

4.2.1. Precipitated silica dispersion

Precipitated silica dispersion was prepared in the small-scale pebble mill which was named as vertical glass pebble mill-1kg. It mills by rotating at a speed of 500 rpm for 30 minutes at room temperature. Vertical Glass Pebble mill is shown in the Figure 4.5.

Figure 4.5- Vertical Glass pebble mill

4.2.2. Fumed silica dispersions

Fume silica dispersion was prepared by using magnetic stirrer named as laboratory magnetic stirrer-1kg. To prepare the dispersion, silica was mixed with water, KOH, Surfynol and silane coupling agent at a speed of 1000 rpm for 20 minutes at room temperature. Due to volatile nature of the dispersion fumed silica was loaded by small amounts until the complete of dispersion preparation. The magnetic stirrer used in the experiment is indicated in the Figure 4.6.

Figure 4.6- Magnetic Stirrer - 1kg

4.3. Preparation of Solutions

4.3.1. Coagulation solution

Coagulation solution was made by mixing 99% calcium nitrate crystals in liquid methanol to a 2% strength. This was done in a simple blade stirrer at a speed of 100 rpm for 15 minutes at room temperature.

4.3.2. Solvent solution

Solvent solution was made by mixing of 99% acetic acid in liquid xylene to a 3.5% strength. This was done in a simple blade stirrer at a speed of 100 rpm for 15 minutes at room temperature.

4.3.3. Calcium water

Calcium water solution was made by mixing of 99% calcium nitrate crystals in water to a 8% strength. This was done in a simple blade stirrer at a speed of 100 rpm for 20 minutes at room temperature.

4.4. Preparation of Compounds

The compound preparation was carried out in two steps. In the first step, basic compound preparation was carried out in simple stirrer machine with capacity of 100kg by mixing low ammonia centrifuge latex, prepared filler material dispersion (calcium carbonate, or precipitated silica, or fumed silica), silane coupling agent (si69), sulfur dispersion, Zinc Oxide dispersion, accelerators, stabilizers and wax as per the receipe design given in Table 6.6 at 100 rpm for 30 minutes and stored in containers until it reached required maturity level. Maturity level was measured through Toluene swelling index test (TSI) and Chloroform test results (CTR) test. Normal maturity level for natural rubber-based compound is 4 days and, in this experiment, it was dragged from 7 to 12 days. Second stage compound was made by adding pigments, sanitizers and thickener materials to basic compound as per the experiments receipe given in Table 6.7 and mixing was done in the same machine with 100 rpm for 15 minutes. All mixing processes were carried out at the room temperature.

4.5. Preparation of Dipped Glove Samples

Glove samples were prepared at the laboratory scale automated dipping line as per the standard dipping specifications. According to this specification, firstly, metal formers with polyester liners were dipped in the prepared coagulation solution and obtained samples secondly were dipped in the prepared latex compound and thirdly they were dipped in solvent solution and finally the samples were dipped in the calcium water solution prior to leaching. All these dipping steps were carried out at room temperature and there was a drying time, approximately 5min, after each dipping.

Then these formers with uncured gloves were leached in hot water bath at 50^0C with addition of 10% of fresh water per each hour for removal of unreacted chemicals. Finally, those gloves were cured in the same dipping line oven at a temperature profile of 80^0C to 120^0C for 46 minutes. The fragment of the dipping line used for the glove sample preparation is indicated in the Figure 4.7.

Figure 4.7-Dipping Line

5. TESTINGS

Various test apparatus and tools were used for raw material testing and glove performance testing. All tests were carried out with calibrated test apparatus and as per the standard laboratory procedures were used in industrial glove manufacturing industry.

5.1.Raw Material Testing

In raw material quality controlling, most of the materials were not analytically tested due to lack of test apparatus and time but based on suppliers' certificate of analysis (COA), or certificate of conformity (COC) reports and experience of supplier-company relationship, materials were accepted. Further some of materials were tested against specific gravity, viscosity, total solid content, color, odor, physical appearance, etc.

5.1.1. Total Solids Content (TSC)

This test was used to analyze non-volatile content at 105 ^{0}C in low ammonia centrifuged latex, dispersions, pigments, and other liquid based compounding ingredients. A sample of 2g from each category was heated at 105 ^{0}C for two hours and it was dried at 70 ^{0}C for 15 minutes intervals until weight get constant. TSC was calculated as remaining weight percentage per initial sample weight.

5.1.2. Dry Rubber Content (DRC)

This test was used to analyze rubber content on low ammonia centrifuged latex. Test was initiated by taking 10g of centrifuged latex sample into a petri dish and secondly distilled water was added until concentration reduced to 20% and thirdly 75 cm^3 of 20 g/dm^3 acetic acid was added for coagulation of rubber. Coagulum was gently depressed and steamed for 15-30 min until all the rubber part coagulate completely. After complete coagulation, coagulum part was pressed gently to expel water and a uniform sheet was obtained. Then the rubber sheet was rinsed for 5 minutes with water and it was dried for 30 minutes intervals at 70 ^{0}C until constant weight was achieved. DRC was calculated as a percentage of remaining weight from initial sample weight.

5.1.3. Mechanical Stability Time (MST)

This test was used to analyze the resistance of the centrifuged latex sample towards mechanical agitation. Test was performed by stirring 100g of centrifuged latex sample at high speed (14,000 ± 200 rev/min) until initiation of flocculum (tiny particles). Time taken for the first appearance of flocculum was taken as MST.

5.1.4. Volatile Fatty Acid (VFA) Number

Volatile fatty acids are developed in centrifuged latex due to degradation of sugar part of the latex and leads to stability and storing ability. VFA test was carried out to measure the volatile fatty acid content of centrifuged latex. Firstly, 50g of latex sample was mixed with 50g of ammonium sulphate solution to coagulate and rubber part was removed. Secondly the serum was filtered, and it was acidified by adding 5cm^3 of the sulfuric acid solution. Thirdly fatty acid was extracted from the serum through the test apparatus by evaporation and distillation. Finally, it was titrated with $Ba(OH)_2$ solution to get the VFA number.

5.1.5. pH

pH levels of dispersions and compounds were measured with pH meter directly. Prior to take any pH reading, meter was calibrated with standard solutions.

5.1.6. Specific Gravity

Specific gravity of methanol and xylene were measured with hydrometer at room temperature.

5.1.7. Weight

Weighing scale Model AY220 was used to measure the weight of the raw material ingredients for dispersions and compound preparation.

5.2.Dispersion Testing

In-house dispersions were made with mixing machines or horizontal pebble mill. Those were tested against Cloud Test, Total Solid Content (TSC), and pH.

5.2.1. Cloud Test

Cloud test was carried out to measure material grinding quality, particle size, dispersion stability and particle size distribution of the dispersion. Cloud test was conducted by dropping a small grinded dispersion material droplet in to a graduated cylinder completely filled with water and letting material to settle freely. Settling time was measured. Over grind dispersions show higher settling time than less grinded dispersion material.

5.3.Compound Testing

Under compound quality controlling, compound homogeneity, mixing time, maturation level, cured compound color and flowability were monitored in each batch. Toluene swelling index (TSI), Chloroform test results (CTR), pH, dipped sample glove color and viscosity parameters were tested under compound testing.

5.3.1. Toluene Swelling Index (TSI)

This test was used to analyze maturity level (pre-vulcanized percentage) of compound. Firstly, coagulant solution treated cardboard circle was dipped in compound sample for 10 seconds and secondly circular coagulum piece from cardboard circle was separated and dried for 30 seconds and finally coagulum piece was dipped in the toluene bath for 45minutes to swell. Dimensional changes of sample diameter were calculated as TSI.

5.3.2. Chloroform Test Results (CTR)

This test was used to analyze maturity level (pre-vulcanized percentage) of the compound. Firstly a known weight of compound sample was taken to a beaker. Secondly same weight of chloroform was added to the beaker and was properly mixed with a glass rod. Thirdly the coagulum was taken out and tested for elasticity (visual inspection).

5.3.3. Dipped Sample Glove Color

This test was performed for coating color verification as shade variation leads to nonconformity of products. Test was performed by dipping of glove liner in compound sample and was cured in the laboratory scale oven. Coating color was compared with authentic sample or pantone color book.

5.3.4. Viscosity

This test was used to analyze flowability, thickness, and sticky nature of the compound. A compound sample of 500ml was taken to a beaker and then correct spindle with required RPM was selected in the Brook field viscometer. Finally viscometer reading was taken.

5.3.5. Tensile Strength

This test was used to analyze tensile strength of cured coating material. Test sample was prepared by firstly dipping ceramic formers in coagulation solution. Secondly ceramic formers were dipped in the compound for 10 seconds and thirdly those were cured in laboratory oven at 120 ^{0}C for 45min. Finally, dumbbell shaped test samples obtained from cured unsupported gloves were tested with universal tensile testing machine (Model- Testometric DBBMTCL-50kg).

5.3.6. Analyzing the Microscopic View

Microscopic view analysis was carried out to study and compare the structural characteristics in samples compounds. This test was conducted through OPTICA B-190 LED microscope.

5.4. Glove Testing

Industrial gloves were tested against mechanical performance evaluation tests under EN388:2016 standard, abrasion resistance, blade cut resistance, tear resistance, puncture resistance, ISO 13997 cut resistance and other performance evaluation glove tests such as Tabor abrasion test, Gurley stiffness test, Clark stiffness test, blooming test, laundry test, grip test and aging test.

5.4.1. Abrasion Resistance

Martindale abrasion tester (Model- M235) was used to determine the abrasion performance of the glove samples. A circular specimen of glove material was abraded under constant pressure with lissajous cyclic motion on planner until the occurance of breakthrough. The resistance to abrasion was measured by the number of rubs or cycles that could be borne by the glove. (BSI Standards Publication, 2016)

Prior to the test, samples were conditioned as per the requirement of BS EN 388:2016 standard. For that, samples were retained at least 24h prior to testing at temperature 23±2 ^{0}C and humidity 50±5 %. Then, four circular test specimens with 38mm diameter were cut from glove palm (Figure 5.1) and were fixed to the holder (Figure 5.2 and Figure 5.3). Then machine bed was set to 180 grit standard sand paper and sample was loaded (Figure 5.4 and Figure 5.5) in to the machine. Then the machine was run until breakthrough occur and the number of cycles for breakage was noted. The breakthrough point was found by frequent observation and listening to sound variations with time, based on experience. Finally, abrasion level was selected as per the Table 5.1 which is defined in EN388: 2016 standard and test was carried out.

Table 5.1-Abrasion level

Mechanical test data	**Mechanical Property**	**Level 1**	**Level 2**	**Level 3**	**Level 4**
Abrasion resistance	Abrasion (**Cycles)**	100<	500<	2000<	8000<

Figure 5.1-Circuler sample cut from the glove palm

Figure 5.2-Fix the sample to the sample clip

Figure 5.3-Fix the sample to the sample holder

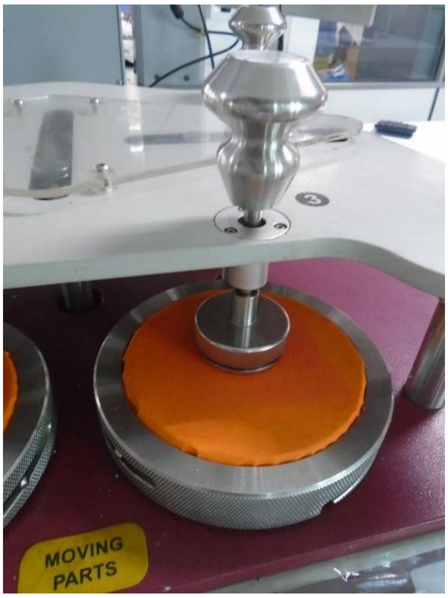


Figure 5.4-Fix the sample holder to Martindale abrasion tester

Figure 5.5-Place load (constant weight) on the top of the fixed sample

5.4.2. Coup Cut Resistance

This test was used to analyze cut resistance performance of industrial glove samples under EN388:2016 standards. A square shaped sample piece was obtained from each cured glove sample and tested through the Coup cut test machine (Model-SPG1616) as per the test standard ISO 13997(TDM test). The sample was conditioned for 24 hours prior to the test at temperature of 23±2 ^{0}C and humidity of 50±5 %.

5.4.3. Tear Resistance

This test was used to analyze tear resistance performance of industrial glove samples under EN388:2016 standards. A trouser shaped sample piece was obtained from cured glove samples and was tested through the universal tensile testing machine. The sample was conditioned for 24 hours prior to the test at temperature of 23±2 ^{0}C and humidity 50±5 %.

5.4.4. Puncture Resistance

This test was used to analyze puncture resistance performance of industrial glove samples under EN388:2016 standards. A circular shaped sample piece was obtained from each cured glove sample and was tested through the universal tensile testing machine. The sample was conditioned for 24 hours prior to testing at temperature 23±2 ^{0}C and humidity 50±5 %.

5.4.5. Tabor Abrasion Resistance

Abrasion performance of coated fabric could be evaluated through the Tabor Abrasion Test, comes under American standard ASTM D3389. Same standards used for evaluating of abrasion performance of industrial gloves (supported gloves). A circular shaped sample piece was obtained from each cured glove sample and was tested through the tabor abrasion testing machine. The sample was conditioned for 24 hours prior to the test at temperature 23±2 ^{0}C and humidity 50±5 %.

5.4.6. Glove Stiffness

Gurley Stiffness Test/ Clark Stiffness Test was used to analyze stiffness of industrial glove samples under TAPPI T 543 standards. The glove sample was directly tested through the Gurley Stiffness Testing/ Clark Stiffness Testing machines. The sample was conditioned for 24 hours prior to the test at temperature 23±2 ^{0}C and humidity 50±5 %.

5.4.7. Grip Test

Grip test was used to evaluate the surface friction with standard objectives in various situations such as dry, wet, oil situations. Test apparatus was designed with various cylindrical probes (wood, metal, glass) with constant weight and was pulled as in Figure 5.6. This test was conducted to get an idea on surface grabbing ability, glove fit, extensibility and flexibility in applications.

Figure 5.6-Grip Test

5.4.8. Aging Test

Aging test was conducted to evaluate aging performance of the glove to decide the service life, allocate warranty period, life cycle evaluation, studding of performance declining patterns, etc. Generally natural rubber-based glove product claiming for three years' service life and synthetic rubber-based glove product claiming for five years' service life. Here aging tests were carried out by aging at 60^0C for 48 hours and was retested for mechanical performance.

5.4.9. Laundry Test

This test was used to analyze launderability of industrial glove. An industrial washing machine was used for the test. The glove sample was sent through a pre-defined washing cycle as 15 min washing in 30 ^{0}C water with washing powder for two cycles and was retested for mechanical performance.

5.4.10. Blooming Test

Most of the natural rubber-based products such as gloves, slippers, tires, carpets are tending to bloom with time and temperature during store in warehouses or showrooms. The main reason for the blooming defect is excess or unreacted chemical availability of the product, and with time and temperature those materials migrate to the surface and appears as milky dusting of dry powder. Glove samples were tested for blooming defect by holding gloves on blooming test box under 40 ^{0}C and atmospheric condition. Visual inspection was carried out on weekly basis.

6. EXPERIMENTAL

Following experiments in the Table 6.1 were planed under this.

Table 6.1- Experiments Plan

#	Experiment	Material Structure
1	Selecting suitable surface modification agent (dispersing agent) for silica reinforcing filler material	Fume silica/ precipitate silica/ ethoxylate (Surfynol)/ Nonylphenol Ethoxylate (N40)/ Naphthalene (Tamol)/ Bentonite clay
2	Replacing $CaCO_3$ non-reinforcing filler material with reinforcing filler material	NR latex/ Fume silica/ precipitate silica/ Surfynol/ $CaCO_3$
3	Optimizing the silica reinforcement filler loading	NR latex/ Fume silica/ precipitate silica/ Surfynol/ $CaCO_3$
4	Optimizing the coupling agent percentage	NR latex/ Fume silica/ precipitate silica/ Surfynol/ $CaCO_3$ / Silane coupling agents

6.1.Experiment 01

This experiment was about selecting a suitable surface modification agent (dispersing agent) for silica reinforcing filler material

Precipitate silica-based dispersions and fume silica-based dispersions based on different dispersion agents were tested through Cloud test to select a suitable surface modification agent (dispersing agent) for the experiment.

Experiment No 1.a

Four type of dispersing agents were used in this experiment, namely, ethoxylate (Surfynol), Nonylphenol Ethoxylate (N40), Naphthalene (Tamol) and Bentonite clay. The batch receipt for the dispersion with precipitated silica is indicated in the Table 6.2. Four dispersion samples with precipitated silica were prepared using above mentioned four types of dispersing agents separately. Two other replication samples were prepared with the same receipt for each type of dispersing agent for better results analysis.

Experiment No 1.b

The same experimental procedure was carried out for Fumed silica also instead of precipitated silica. The batch receipt for the dispersion with fumed silica is indicated in the Table 6.3.

Table 6.2-Batch receipt for selecting dispersing agent with Precipitated silica

Ingredient	**Batch receipt (g)**
Soft Water	745
Stabilizer- KOH	Until pH reached 8.5-11.5
Dispersing agent/ Test variant	2.5
Precipitated Silica with particle size 20 – 200 microns	250
Silane coupling agent-Si 69	2.5
Glass Beads	1000

Table 6.3-Batch receipt for selecting dispersion agent with fume silica

Ingredient	Batch receipt (g)
Soft Water	745
Stabilizer- KOH	Until pH reached 8.5-11.5
Dispersing agent/ Test variant	2.5
Aerosil with particle size 5-50 microns	250
Silane coupling agent-Si 69	2.5
Glass Beads	1000

6.2.Experiment 02

This experiment was about replacing $CaCO_3$ non-reinforcing filler material with reinforcing filler material and optimizing the loading levels.

In traditionally used formulation latex compound was filled with calcium carbonate. Precipitated silica load was varied from 0 to 20 PHR as given in the Table 6.4.

Table 6.4-Precipitated silica loading plan

Sample	1a	2a	3a	4a	5a
Precipitated silica loading	0 PHR	5 PHR	10 PHR	15 PHR	20 PHR

Fumed silica load was varied from 0 to 20 PHR as given in the Table 6.5.

Table 6.5-Fume silica loading plan

Sample	1b	2b	3b	4b	5b
fume silica/ Aerosil	0 PHR	5 PHR	10 PHR	15 PHR	20 PHR

Five samples from compound consisting of precipitated silica dispersion and five samples from compound consisting of fumed silica dispersion were prepared as mentioned in the Table 6.6 and Table 6.7. The same experiment was replicated three more times for each loading level for each type of silica.

Table 6.6- Basic compound

Component in Basic compound	Loading level PHR
Centrifuge latex	Company specific ratio
SBR Latex	Company specific ratio
Nitrile basic	Company specific ratio
KOH-Stabilizer	Company specific ratio
Lauric acid-Stabilizer	Company specific ratio
Freezil- Antifoam	Company specific ratio
Sulfur -Curing agent	Company specific ratio
Set Sit- Accelerator	Company specific ratio
Zinc Oxide - Activator	Company specific ratio
Sanitized- antibacterial	Company specific ratio
Silica- Reinforcement filler	Test variant

Table 6.7-Second stage compound

Component in Second stage compound	Loading level PHR
Basic Compound	Company specific ratio
Pigments- KROMACRYL Blue 4177/ KROMACRYL MIC WHITE	Company specific ratio
Thickener- Acrosole	Company specific ratio

6.3.Experiment 03

Further optimizing the silica reinforcement filler loading

The range of the loading level was reduced, and the loading level was optimized further to gain more accurate results and to select the best silica material from precipitated silica and fumed silica.

Precipitated silica load was varied from 0 to 10 PHR as given in Table 6.8.

Table 6.8-Precipitated silica loading

Sample	1	2	3	4	5
Precipitated silica loading	0 PHR	5 PHR	7 PHR	9 PHR	10 PHR

Fumed silica load was varied from 0 to 10 PHR as given in Table 6.9.

Table 6.9- Fume silica loading

Sample	1	2	3	4	5
fumed silica/ Aerosil	0 PHR	5 PHR	7 PHR	9 PHR	10 PHR

Glove samples were prepared with the basic compounding receipt given in Table 6.10 and secondly compound receipt is given in Table 6.11. Five samples from compound consisting of precipitated silica dispersion and five samples from compound consisting of fumed silica dispersion were prepared as mentioned in the Table 6.10 and Table 6.11. The same experiment was replicated three more times for each loading level for each type of silica.

Table 6.10-Basic compound

Component in Basic compound	Loading level PHR
Centrifuge latex	Company specific ratio
SBR Latex	Company specific ratio
Nitrile basic	Company specific ratio
KOH-Stabilizer	Company specific ratio
Lauric acid-Stabilizer	Company specific ratio
Freezil- Antifoam	Company specific ratio
Sulfur -Curing agent	Company specific ratio
Set Sit- Accelerator	Company specific ratio
Zinc Oxide - Activator	Company specific ratio

Sanitized- antibacterial	Company specific ratio
Silica- Reinforcement filler	Test variant

Table 6.11-Second stage compound

Component in Second stage compound	Loading level PHR
Basic Compound	Company specific ratio
Pigments- KROMACRYL Blue 4177/ KROMACRYL MIC WHITE	Company specific ratio
Thickener- Acrosole	Company specific ratio

6.4.Experiment 04

Optimizing the coupling agent percentage.

Reinforcing silica filler incorporated compound gives better abrasion resistance performance with presences of adequate silane coupling agents in the system. If coupling agents are inadequate in the system, it leads to low density of filer to polymer bonds and poor abrasion performance. On the other hand, excess coupling agents lead for filler coagulation, inhomogeneity of compound and processing difficulties. Therefore, optimization of silane coupling agent in natural rubber-based silica filled compound is importance in commercial production

In this experiment reinforcing filler loading percentage was kept fixed at 7 PHR and silane coupling agent level varied.

Silane coupling agent was dosed from 2 to 10 PHR as given in Table 6.12.

Table 6.12-Silane coupling agent loading

Sample	1	2	3	4	5
Silane coupling agent	2 PHR	4 PHR	6 PHR	8 PHR	10 PHR

The range of the dosing level was reduced, and the dosing level was optimized further to gain more accurate results.

Silane coupling agent was dosed from 0.25 to 1.5 PHR as given in Table 6.13.

Table 6.13-Silane coupling agent loading for optimizing

Sample	1	2	3	4	5	6
Silane coupling agent	0.25 PHR	0.5 PHR	0.75 PHR	1.0 PHR	1.25 PHR	1.5 PHR

Glove samples were prepared with the basic compounding receipt given in Table 6.14 and secondly compound receipt given in Table 6.15. Five samples were prepared in where silane coupling agent was varied according to the Table 6.12. The same experiment was replicated three more times for each loading level for each type of dosing level for more accurate results. Then to optimize the silane coupling agent dosing level further another six samples were prepared with lesser dosing level range as given in Table 6.13. For better results the same procedure was replicated for three more samples for each dosing level.

Table 6.14- Components in basic compound

Component in Basic compound	Loading level PHR
Centrifuge latex	Company specific ratio
SBR Latex	Company specific ratio
Nitrile basic	Company specific ratio
KOH-Stabilizer	Company specific ratio
Lauric acid-Stabilizer	Company specific ratio
Freezil- Antifoam	Company specific ratio
Sulfur -Curing agent	Company specific ratio
Set Sit- Accelerator	Company specific ratio
Zinc Oxide - Activator	Company specific ratio
Sanitized- antibacterial	Company specific ratio
Silica- Reinforcement filler	Optimized value

Table 6.15-Components in second stage compound

Component in Second stage compound	Loading level PHR
Basic Compound	Company specific ratio
Old Compound	Company specific ratio

Pigments- KROMACRYL Blue 4177/ KROMACRYL MIC WHITE	Company specific ratio
Thickener- Acrosole	Company specific ratio

7. RESULTS AND DISCUSSION

7.1.Samples

Glove samples made during the experiments are shown in the Figure 7.1, Figure 7.2, Figure 7.3, Figure 7.4 and Figure 7.5.

Figure 7.1-Experiment-02, Precipitate silica-based glove sample

Figure 7.2-Experiment-02, Fume silica-based glove sample

Figure 7.3-Experiment-03, Precipitate silica-based glove sample

Figure 7.4-Experiment-03, Fume silica-based glove sample

Figure 7.5-Experiment-04, Fume silica/ Coupling agent-based glove sample

7.2.Experiment 01

Selecting suitable surface modification agent (dispersing agent) for silica reinforcing filler material

Results of Cloud test are indicated in Figure 7.6 and Figure 7.7 graphical presentation of results is included in Figure 7.8.

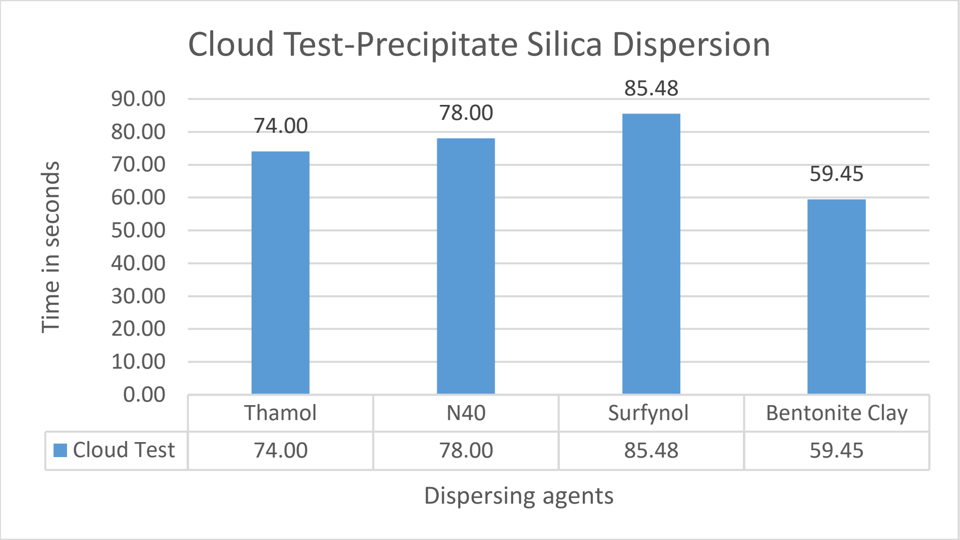


Figure 7.6-Cloud Test-Precipitate Silica Dispersion

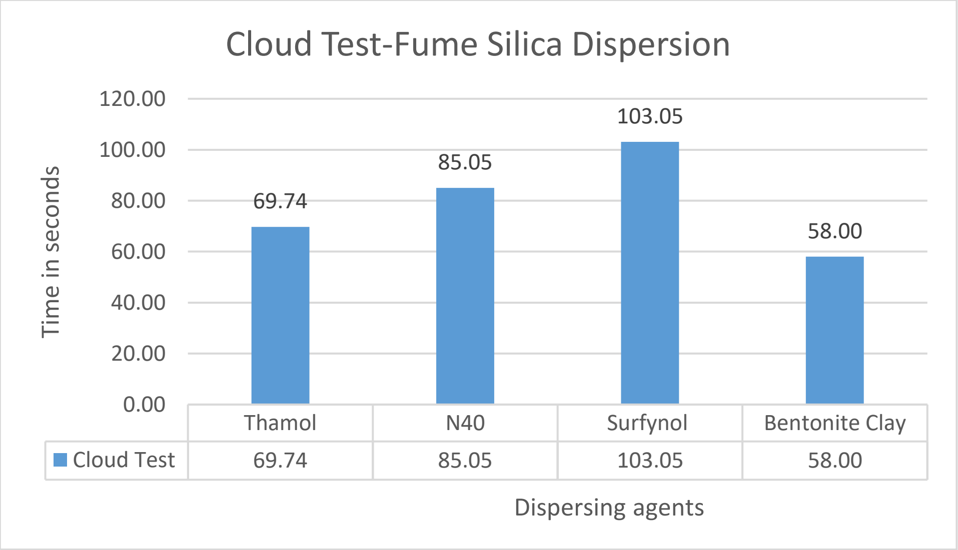
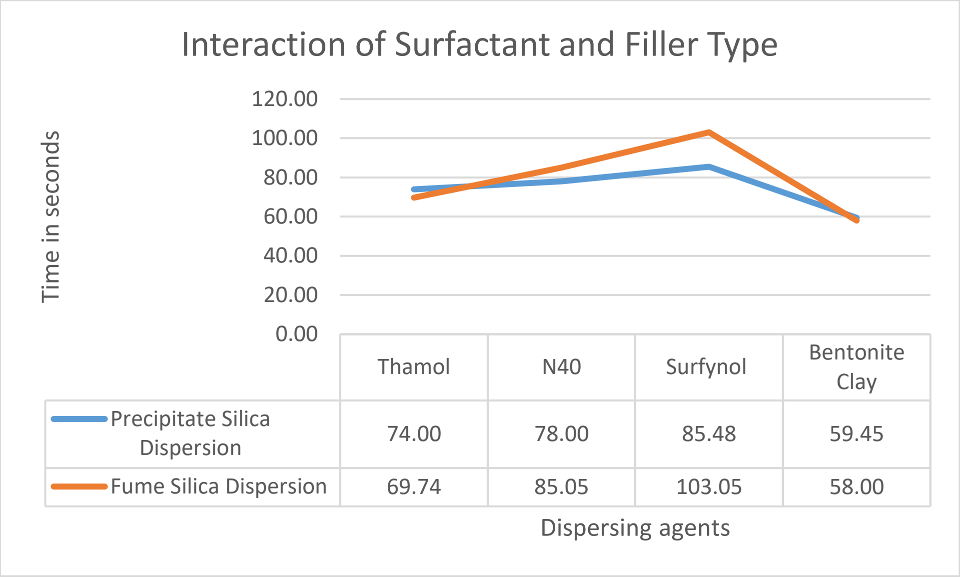


Figure 7.7-Cloud Test-Fume Silica Dispersion



	Thamol	N40	Surfynol	Bentonite Clay
Precipitate Silica Dispersion	74.00	78.00	85.48	59.45
Fume Silica Dispersion	69.74	85.05	103.05	58.00

Figure 7.8-Interaction of Surfactant and Filler Type

As per the cloud test result of Experiment-01, Surfynol dispersion agent shows better stability in both precipitated silica-based dispersion as well as fume silica-based dispersion. Accordingly, all following experiments were carried out with Surfynol dispersion agents.

7.3.Experiment 02

Replacing $CaCO_3$ non-reinforcing filler material with reinforcing filler material and optimizing the loading levels.

Test results of experiment 02 are indicated in Figure 7.9, Figure 7.10 and graphical presentation of results is included in Figure 7.11.

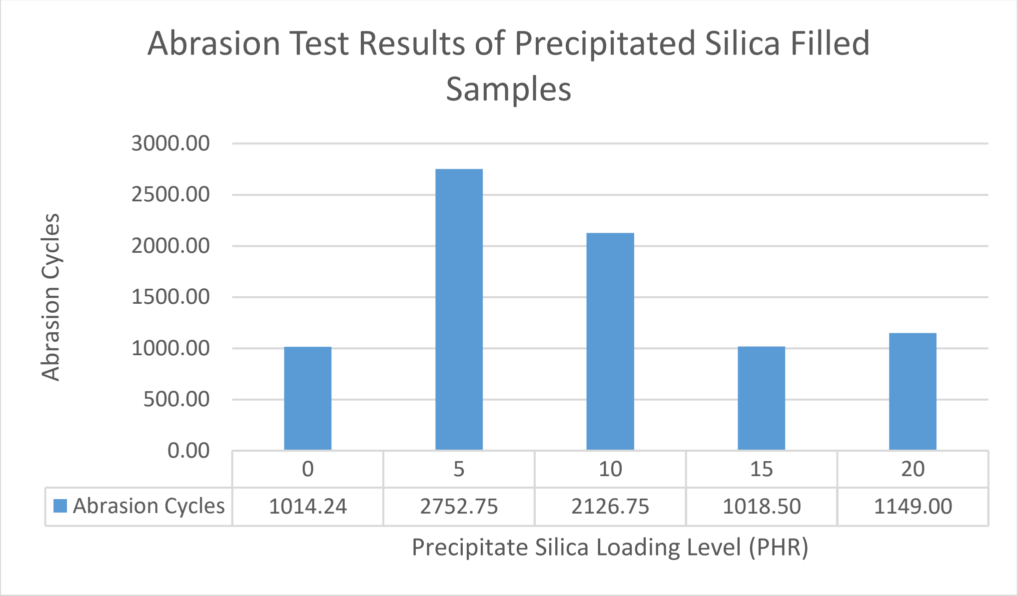


Figure 7.9-Abrasion Test Results of Precipitated Silica Filled Samples

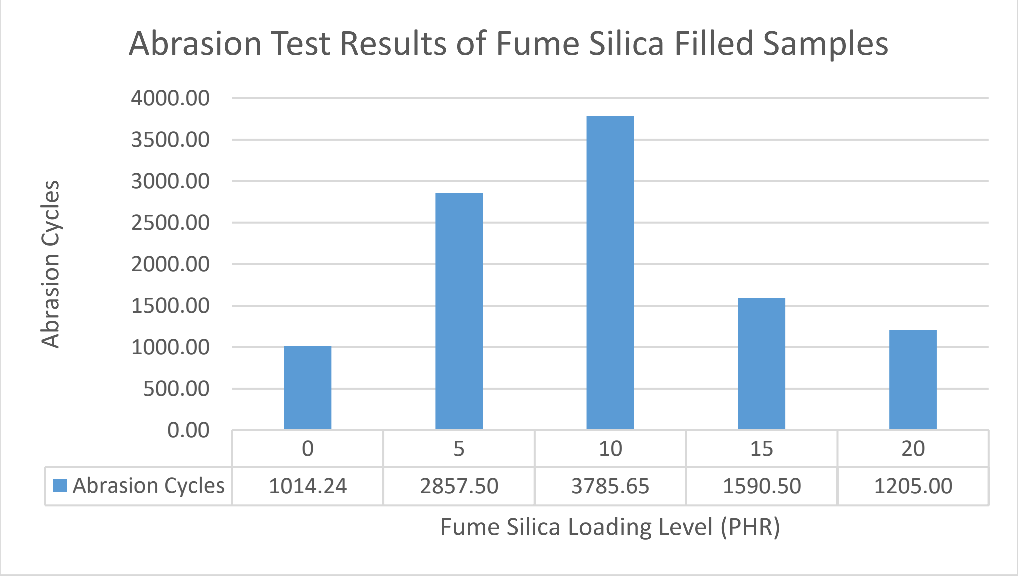
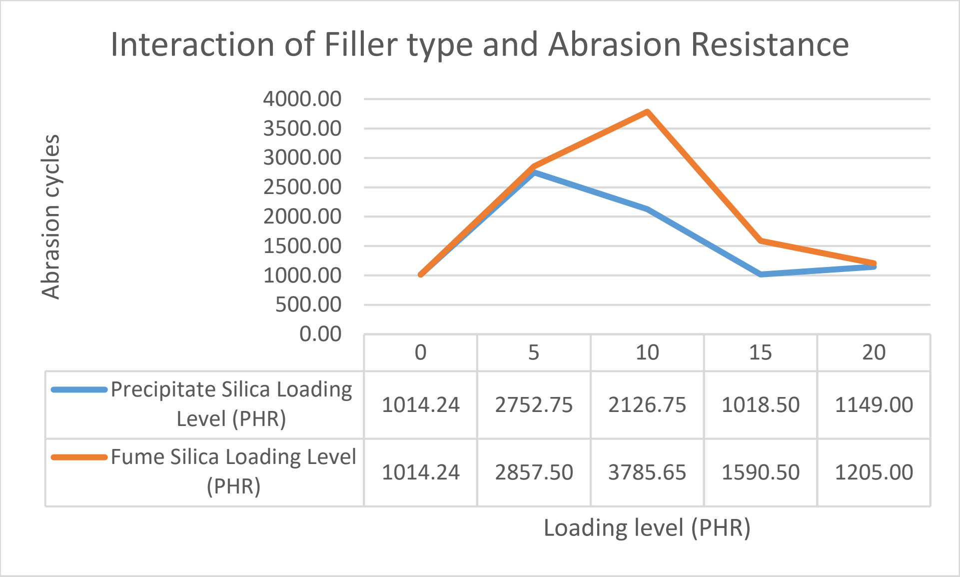


Figure 7.10-Abrasion Test Results of Fume Silica Filled Samples



	0	5	10	15	20
Precipitate Silica Loading Level (PHR)	1014.24	2752.75	2126.75	1018.50	1149.00
Fume Silica Loading Level (PHR)	1014.24	2857.50	3785.65	1590.50	1205.00

Figure 7.11-Interaction of Filler type and Abrasion Resistance

Abrasion resistance of polymer-based composite materials were improved with addition of reinforcing filler as inter molecular attractions increased in the compound. According to the result of experiment 02, adding silica based reinforcing filler materials in to the compound has given better abrasion performance than non-reinforcing filler calcium carbonate loaded compound. Further results show better abrasion performance could be obtained from fume silica-based compound than precipitated silica-based compounds. Fume silica loaded samples show gradual improvement in abrasion performance up to loading level of 10 PHR and declined with further loading while showing maximum abrasion resistance performance at around 10 PHR. Meanwhile precipitated silica loaded samples show gradual improvement up to 5 PHR and declining hereafter through the maximum performance at 5 PHR.

7.4. Experiment 03

Further optimizing the silica reinforcement filler loading

Test results of experiment 03 are mentioned in Figure 7.12, Figure 7.13 and graphical presentation of results is included in Figure 7.14.

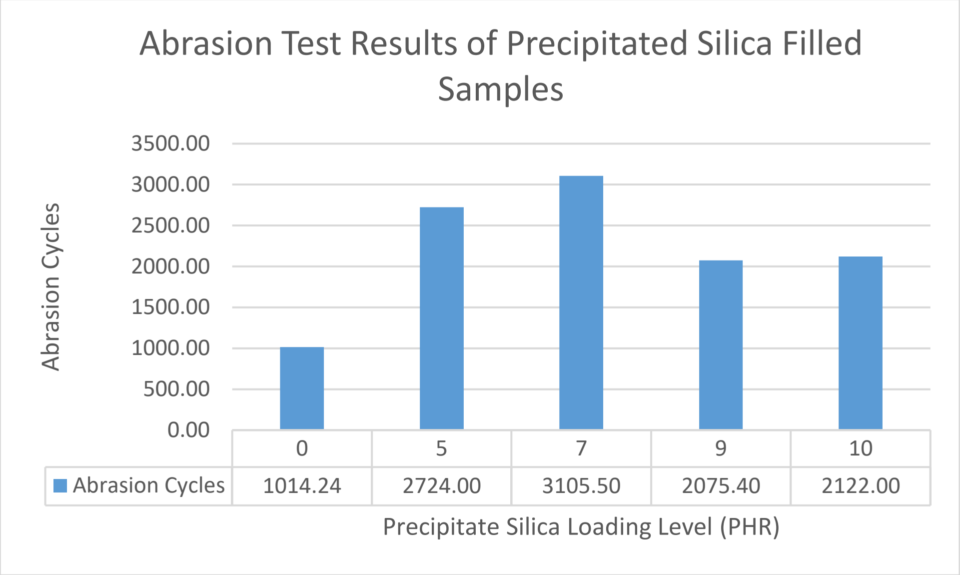


Figure 7.12-Abrasion Test Results of Precipitated Silica Filled Samples

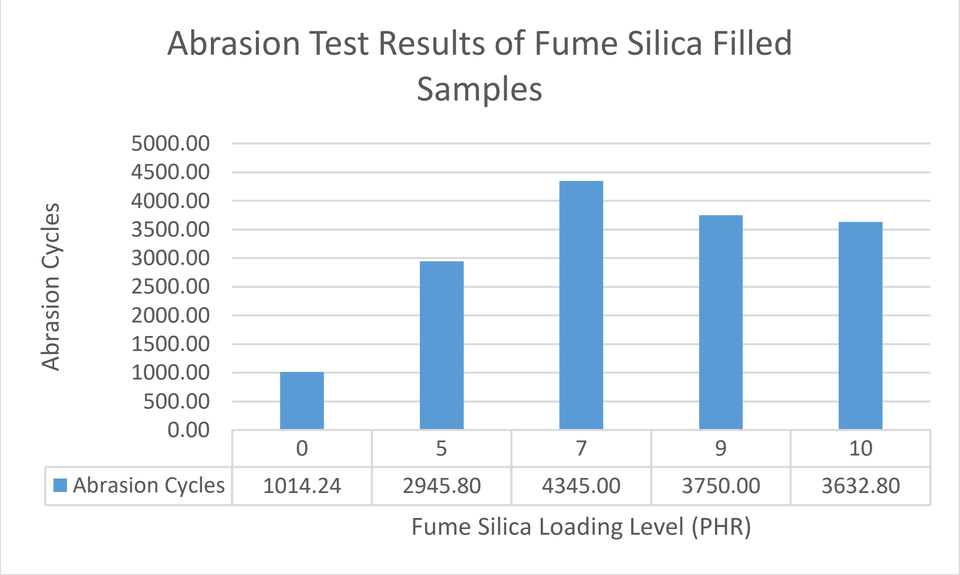
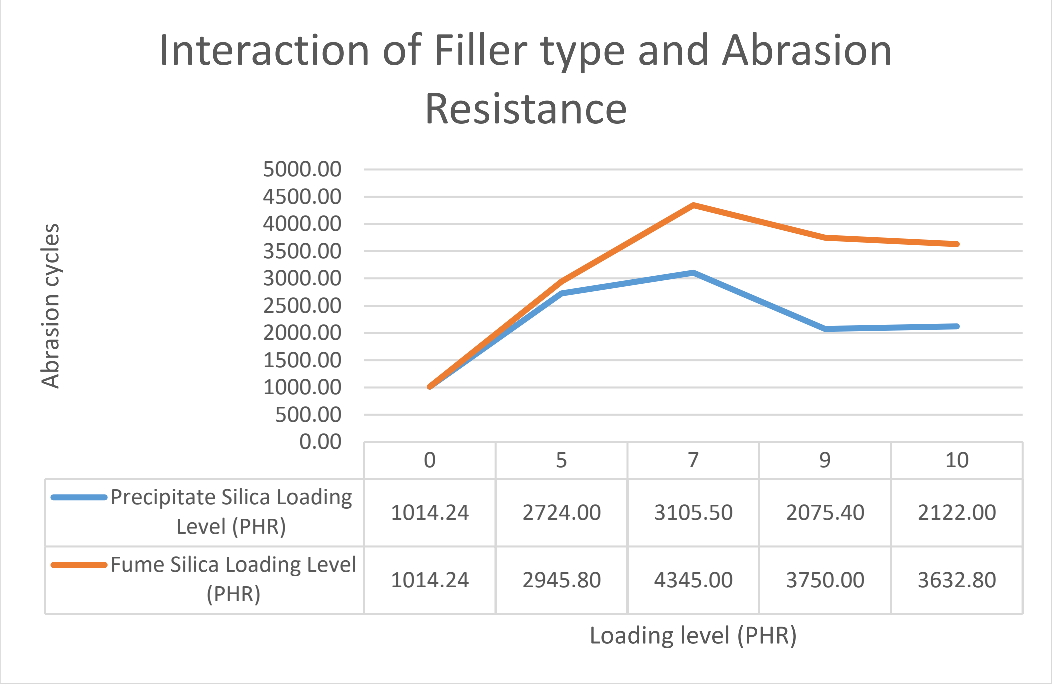


Figure 7.13-Abrasion Test Results of Fume Silica Filled Samples



	0	5	7	9	10
Precipitate Silica Loading Level (PHR)	1014.24	2724.00	3105.50	2075.40	2122.00
Fume Silica Loading Level (PHR)	1014.24	2945.80	4345.00	3750.00	3632.80

Figure 7.14-Interaction of Filler Type and Abrasion Resistance

As per the Figure 7.14, optimized abrasion resistance was obtained with 7% loading of both precipitated silicas loaded samples and fume silica loaded samples. The abrasion resistance improvement in this experiment of natural rubber based industrial glove was 8 times from typical average of 500 cycles to typical average of 4000 cycles. According to mechanical performance standard for industrial glove, improved performance gives abrasion resistance level 3 whereas previous result was level 2.

7.5. Experiment 04

Optimizing the coupling agent percentage.

Test results of experiment 04 are mentioned in Figure 7.15, and Figure 7.16.

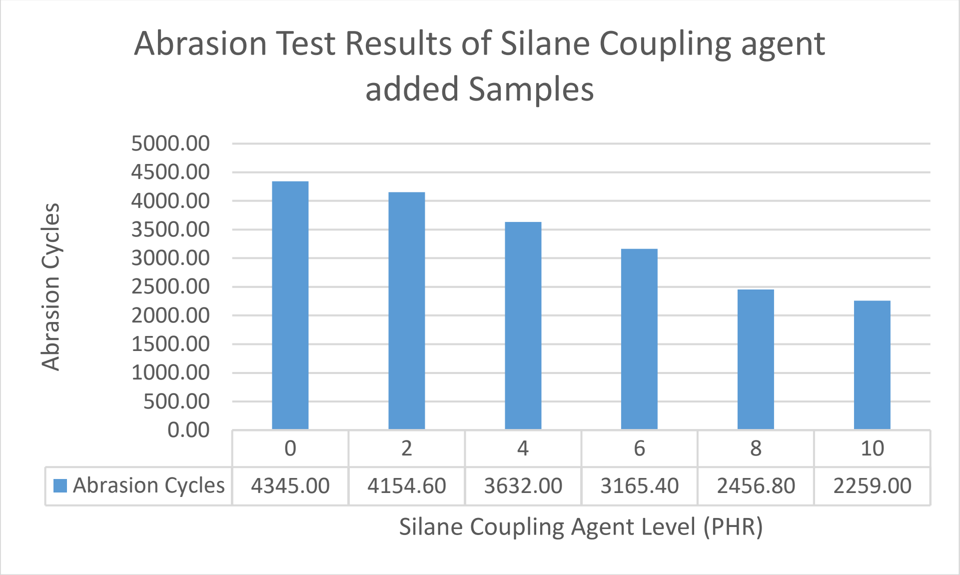


Figure 7.15-Abrasion Test Results of Silane Coupling agent added Samples

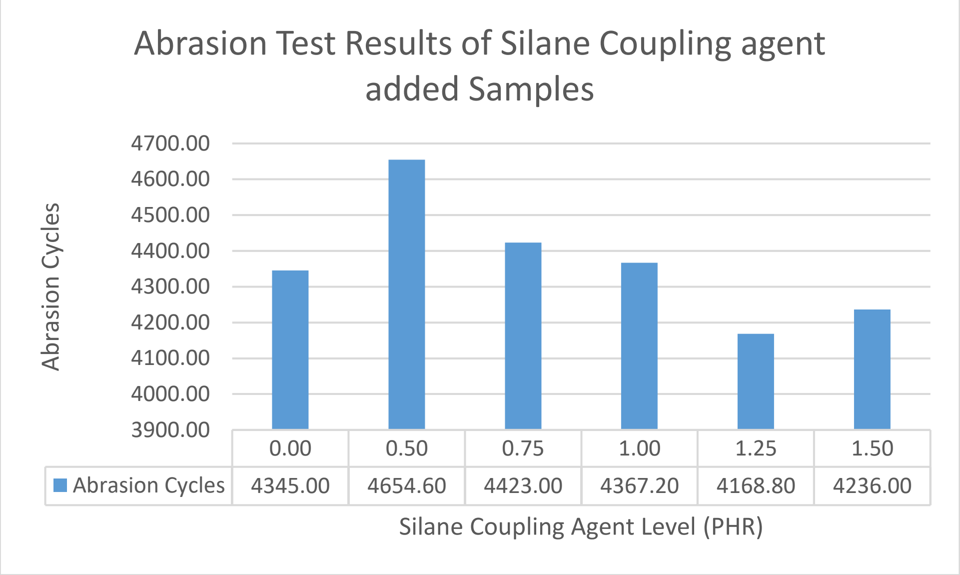


Figure 7.16-Abrasion Test Results of Silane Coupling agent added Samples

Based on Figure 7.15, it can be concluded that adding excess silane coupling agents in to profile leads to declining of abrasion performance of the polymer articles and best performance could be obtained within 0 to 2 PHR levels. As per Figure 7.16, further optimization of silane coupling agent in the natural rubber based liquid compound could be seen in 0.5 PHR level. Accordingly, abrasion performance of natural rubber based industrial glove could be optimized through the incorporation of fume silica reinforcing filler 7 PHR and silane coupling agent 0.5 PHR in to system.

7.6. Product Change Validation

Product change validation in all aspects prior to have commercial production and while commercial production runs, are mandatory in personal protective equipment manufacturing industry. There are many test methods and criterions applying for industrial glove validation and related test methods and results are described here.

7.6.1. Tensile Test

Test results of tensile test experiments are mentioned in Figure 7.17, Figure 7.18 and Figure 7.19.

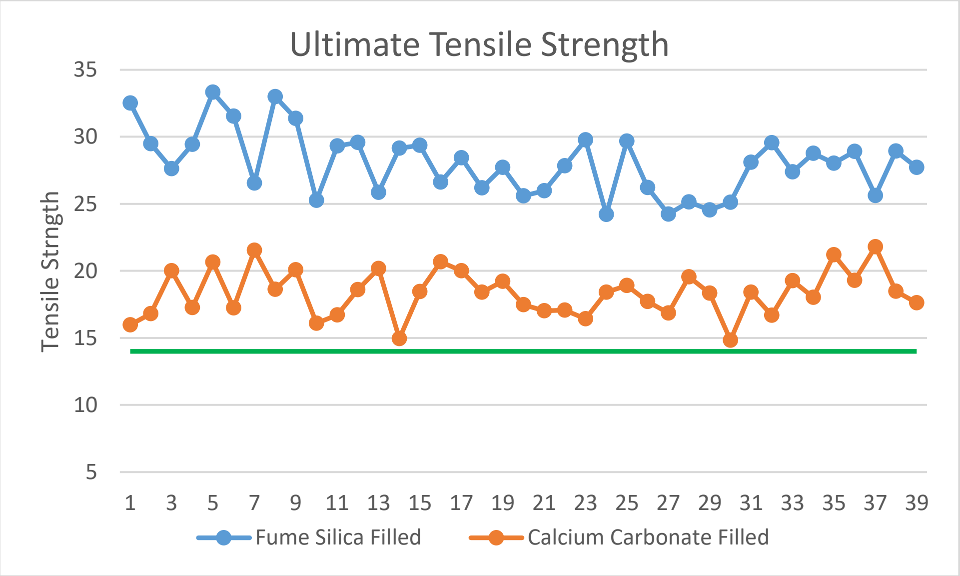


Figure 7.17-Ultimate Tensile Strength

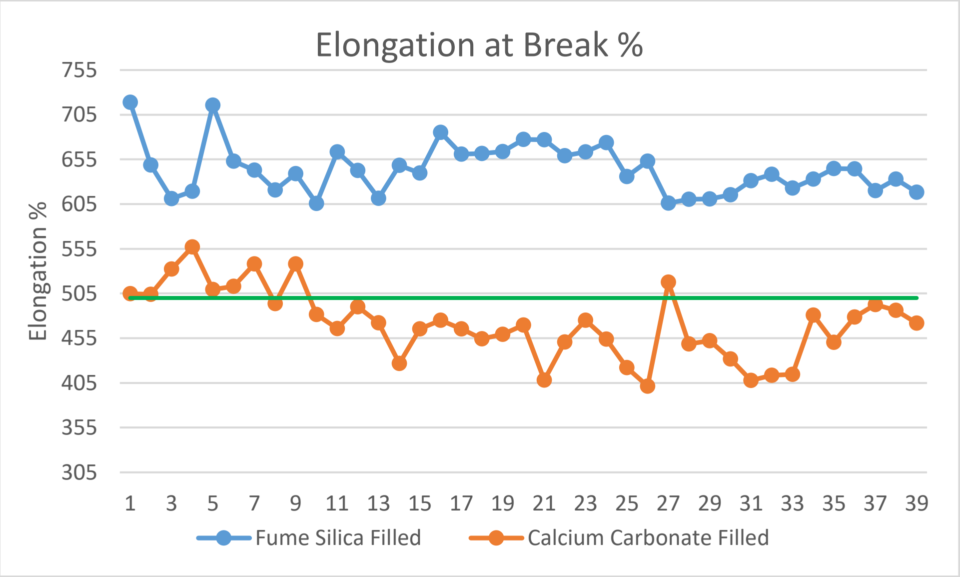


Figure 7.18-Elongation at Break %

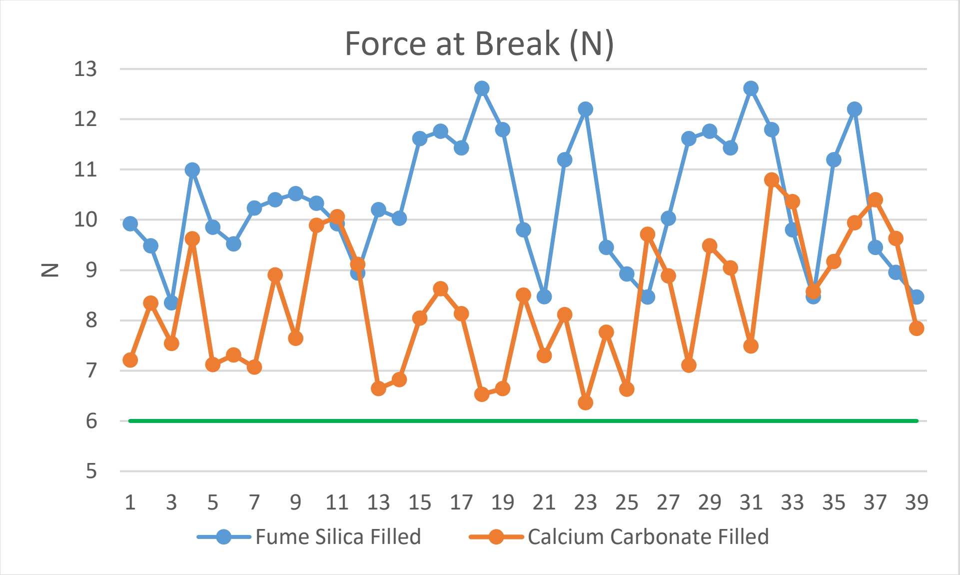


Figure 7.19-Force at Break

Under tensile test, ultimate tensile strength, elongation percentage at brake and force at brake were evaluated for previous compound receipt and developed compound receipt. Test results shows property enhancement in all three parameters from considerable level of value and low deviational risk with parameter specifications.

7.6.2. Abrasion Resistance Test

Abrasion resistance performance of production run samples from before modification and after modification were analyzed as bellow Figure 7.20. Based on the results, average abrasion performance with calcium carbonate filled gloves is 600 cycles while fume silica filled gloves is 3800 cycles and performance gain is six times.

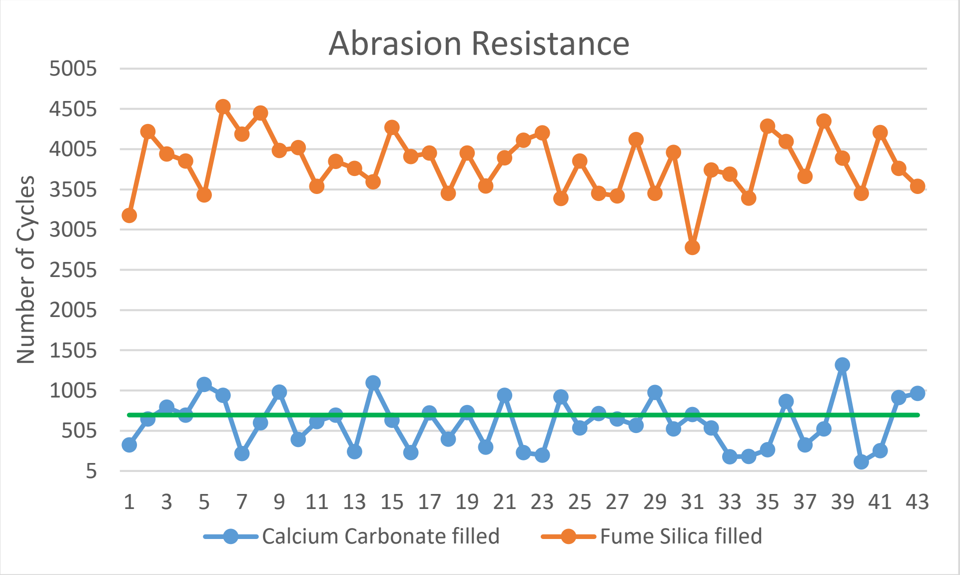


Figure 7.20-Abrasion Resistance

7.6.3. Cut Resistance Test

Cut resistance performance analysis with calcium carbonate filed samples and fume silica filled samples were carried out and results shows on Figure 7.21. According to the graph, compound receipt modification has no significant impact for the cut resistance performance but shows slight improvement and reduction of performance failure risk further. As cut performance contributed by both coting as well as liner performance and same liner use for both experiments shows no significant improvement but shows slight improvement due to coating performance improvement with modification.

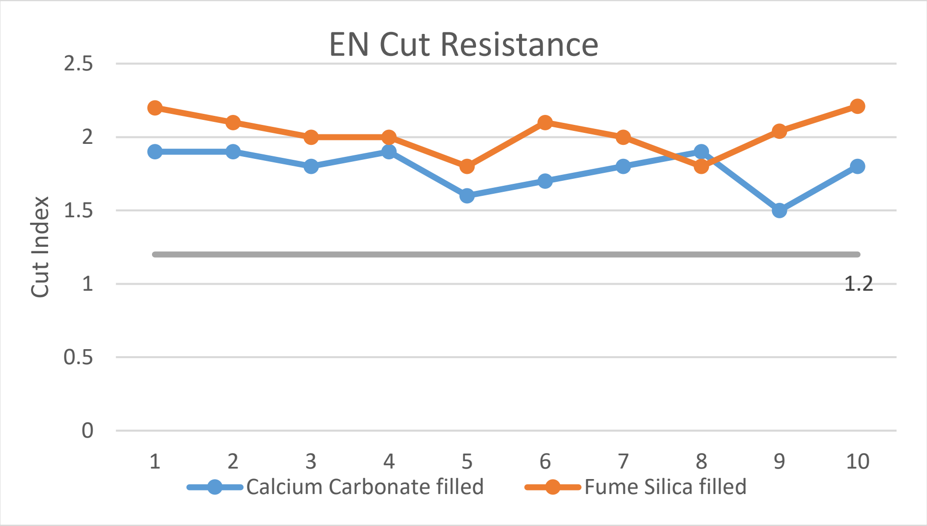


Figure 7.21-EN Cut Resistance

7.6.4. Tear Resistance Test

Tear resistance performance analysis in-between calcium carbonate filled glove samples and fume silica filled glove samples are indicated in Figure 7.22. Tear resistance performance also mainly depends on liner performance as well as coating performance, but majority from the liner. In this experiment same liner was used for both non-reinforcing fillers filled compound and reinforcing fillers filled compound and tear performance tested through the universal tensile testing machine. As per the test results, no significant improvement in tear resistance on modified compound, but slight improvement with reinforcing effect of fume silica.

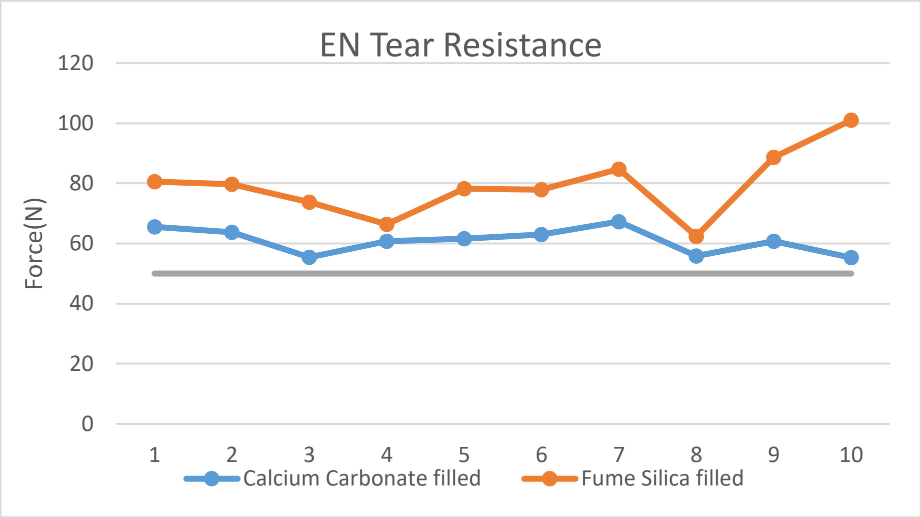


Figure 7.22-EN Tear Resistance

7.6.5. Puncture Resistance Test

Puncture resistance performance of calcium carbonate filler filled glove samples and fume silica filler filled glove samples were tested and results were analyzed in Figure 7.23. Similar as previous properties, only a slight improvement in puncture resistance performance of reinforcing filler loaded glove samples can be seen, compared to non-reinforcing filler loaded glove samples. Puncture resistance performance mainly depends on liner characteristics as well as coating characteristics. As the same liner was used for both experiments, no significant improvement was seen in the results analysis.

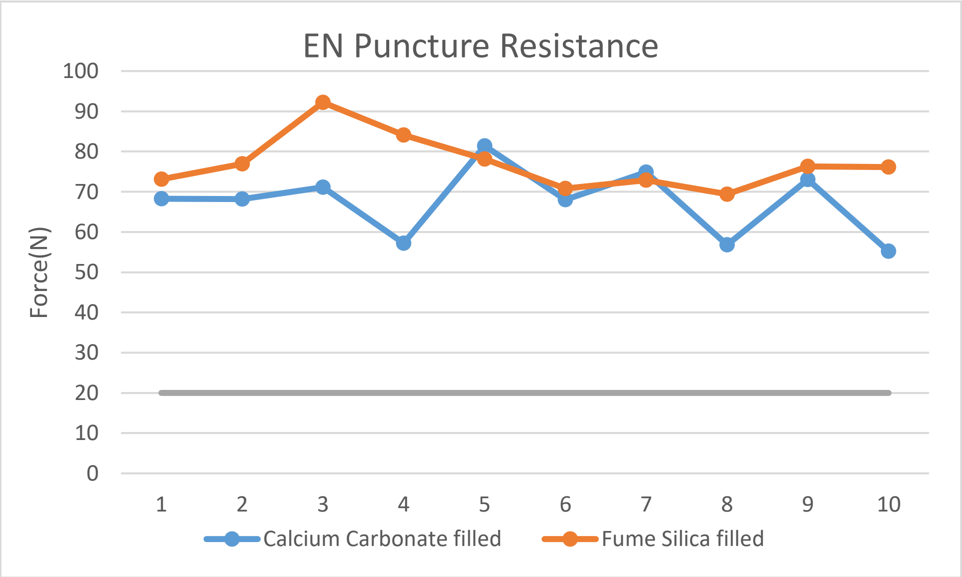


Figure 7.23-EN Puncture Resistance

7.6.6. Tabor Abrasion Resistance Test

Tabor abrasion test was carried out for performance evaluation of non-reinforcing filler filed glove samples and reinforcing filler filled gloves samples and results were analyzed in Figure 7.24. As per the analysis, it shows significant improvement of abrasion performance of fume silica filler filled glove samples compare to calcium carbonate filer filled glove samples due to reinforcing effect of filler.

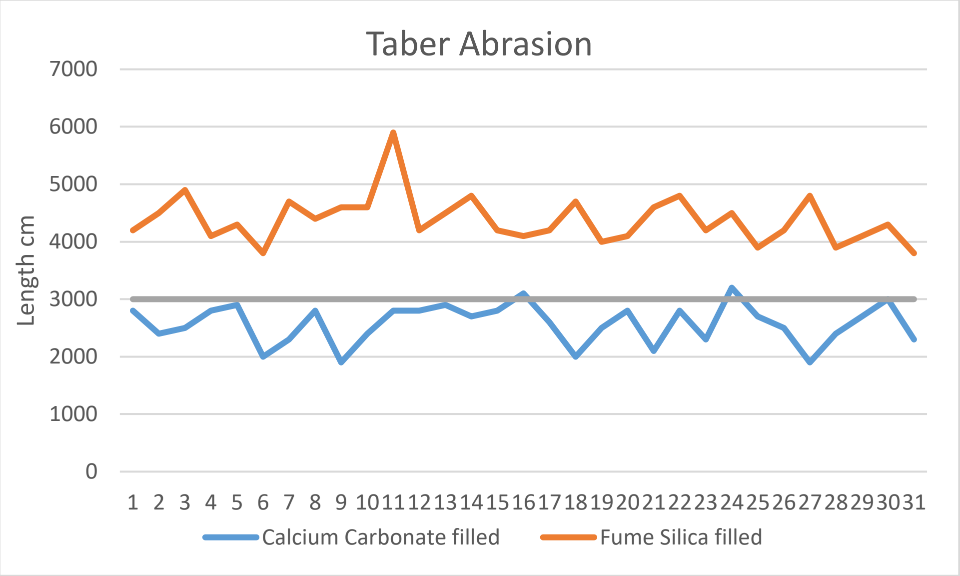


Figure 7.24-Taber Abrasion Resistance

7.6.7. Gurley Stiffness Test/ Clark Stiffness Test

Gurley stiffness test and Clark stiffness test were carried out for analysis of stiffness performance of non-reinforcing material filled glove samples and reinforcing filler filled gloves samples and results are as in Figure 7.25 and Figure 7.26. As per the analysis, stiffness characteristics has increased of reinforcing filler material filled samples compared to non-reinforcing material filled glove samples due to increase of intermolecular bonding density. This can be considered as a negative impact of the experiment as increased glove stiffness and hardness cause reduced glove comfortability.

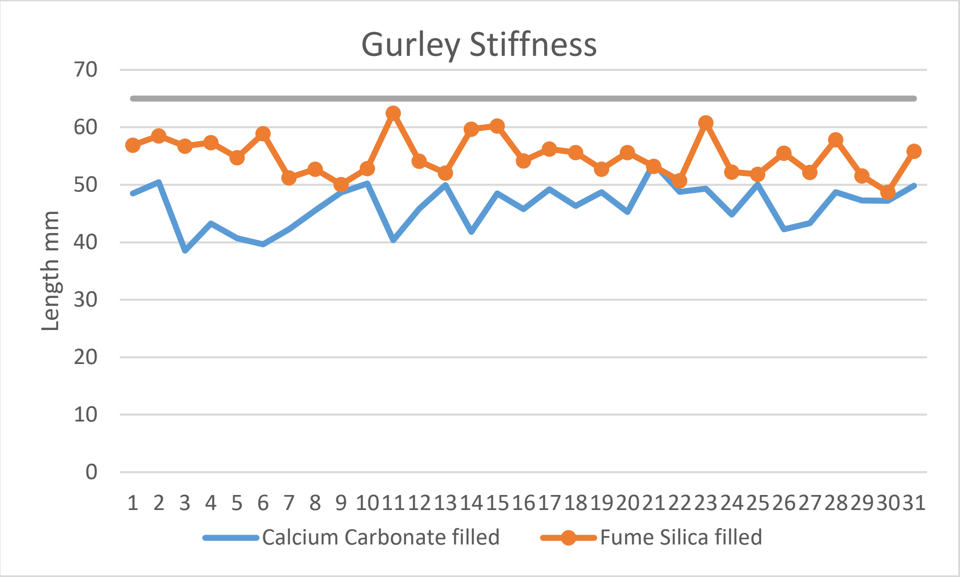


Figure 7.25-Gurley Stiffness

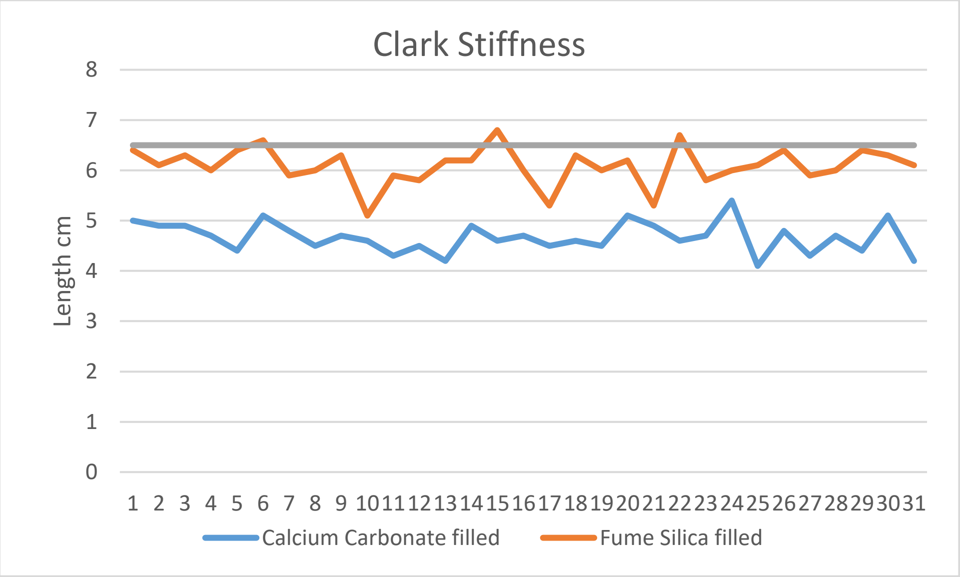


Figure 7.26-Clark Stiffness

7.6.8. Grip test

Grip test summary is shown in Table 7.1 and Table 7.2 related to non-reinforcing filler filled glove samples and reinforcing filler filled glove samples. As per the test analysis natural rubber-based glove with usual coating and modified coating have no impact for the grip as both gloves are suitable for any dry applications and wood and metal based wet applications.

Table 7.2-Grip test Summary-Calcium carbonate filled glove sample

Grip	Wood	Metal	Glass
Dry	√	√	√
Wet	√	√	×
Oil	×	×	×

Table 7.1-Grip test Summary-Fume Silica filled glove sample

Grip	Wood	Metal	Glass
Dry	√	√	√
Wet	√	√	×
Oil	×	×	×

7.6.9. Laundry Test

Test results mentioned in Table 7.3 and results shows launderability performance of fume silica filled glove samples are lesser than calcium carbonate filled glove samples due to high stiffness behavior.

Table 7.3-Laundry Test

Mechanical performance	Calcium carbonate filed glove samples			Fume silica filled glove samples		
	Before laundry	After laundry	Change %	Before laundry	After laundry	Change %
Abrasion resistance	601.90	560.50	6.88%	3825.34	1784.25	53.36%
Cut resistance	1.78	1.45	18.54%	2.025	1.69	16.54%
Tear resistance	60.91	59.46	2.38%	79.34	63.74	19.66%
Puncture resistance	67.41	54.36	19.36%	76.99	52.34	32.02%
Tabor abrasion resistance	2570	1867	27.35%	3674	1764	51.99%

7.6.10. Blooming Test

Glove samples from reinforcing filler filed compound and non-reinforcing filer filled compound were tested for blooming defect by holding gloves on blooming test box under 40 ^{0}C and atmospheric condition and visual inspection were carried out weekly basis. Test results of blooming test are mentioned in Table 7.4 and shows lower blooming tendency on fume silica filled glove samples compared to calcium carbonate filled glove samples due to high density of inter molecular bonding.

Table 7.4-Blooming Test

Blooming test	Calcium carbonate filled glove samples	Fume Silica filled glove samples
1st week	No blooming effect	No blooming effect
2nd week	No blooming effect	No blooming effect
3rd week	Coating color getting mat	No blooming effect
4th week	Slight blooming on the finger tips	No blooming effect
5th week	Milky dusting appearance on the finger area	Coating color getting mat
6th week	Dry powder appearance on the fingers and slight blooming on the palm area	Slight blooming on the finger tips
7th week	Dry powder appearance	Slight blooming on the finger tips
8th week	Dry powder appearance	Slight blooming on the finger tips

7.6.11. Aging Test

Aging tests were carried out for calcium carbonate filler filled natural rubber-based glove samples and fume silica filler filled natural rubber-based glove samples by aging at 60^0C for 48 hours. Test results are mentioned in Table 7.5. According to the test results, reinforcing filler filled glove samples gives better performance with time than non-reinforcing filler filled glove samples.

Table 7.5-Aging Test

Mechanical performance	Calcium carbonate filed glove samples		Fume silica filled glove samples	
	Before aging	After aging	Before aging	After aging
Abrasion resistance	601.90	350.40	3825.34	2954.25
Cut resistance	1.78	1.63	2.025	1.75
Tear resistance	60.91	54.64	79.34	70.64

Puncture resistance	67.41	61.24	76.99	64.45
Tabor abrasion resistance	2570	1250	3674	2725

7.7.Microscopic Analysis

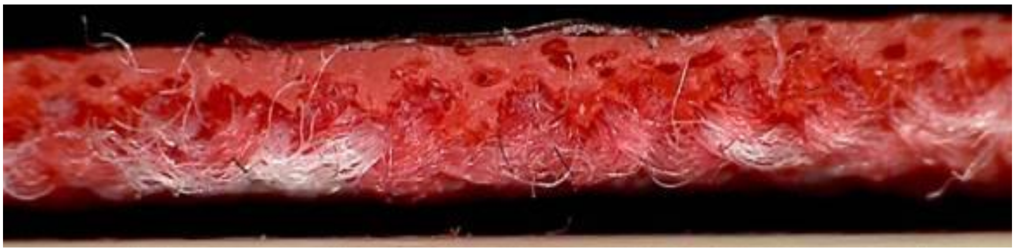


Figure 7.27-Cross Section-Calcium carbonated filler loaded glove sample

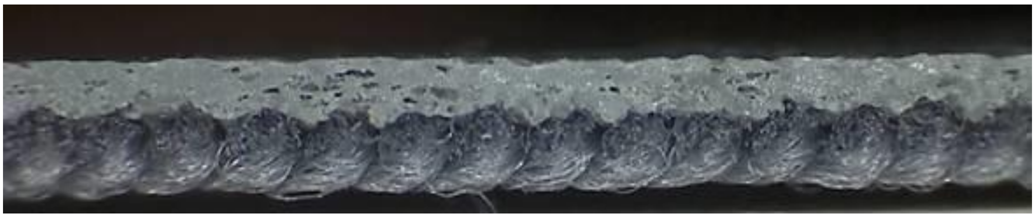


Figure 7.28-Cross Section-Fume Silica filler loaded glove sample

The Figure 7.28 shows the structure of fume silica filler loaded glove sample. A clearly seen dense interface structure could be a result of good bonding between components. When compared to the same filled with calcium carbonate filler, the structure looks more lose that could be arisen from poor compatibility of components, Figure 7.27. Calcium carbonate filler loaded structure has many voids in between the particles which reduce the strength and the abrasion. The structure of the fume silica loaded glove sample is closely packed and properly bonded to the liner with less voids which indicates the higher strength as well as higher abrasion.

In overall, compared to the calcium carbonate filler loaded glove sample, fume silica loaded glove sample cross section could indicate on better mechanical performance and reliable characteristics.

8. CONCLUSIONS

1.It was found that abrasion resistance of industrial gloves made out filled natural rubber latex compounds depends on number of factors such as coagulation strength, type of reinforcing filler used, surface characteristics of the filler namely particle size, filler content, presence of coupling agent and curing percentage. The most important parameters out of them as it was found in this research were type of filler, filler loading, particle size of the used filler and its ability to form strong inter-chain bonds across rubber -filler interface with application of silane coupling agent.

2. It was found that abrasion performance of industrial gloves made out filled natural rubber latex compounds depends on filler loading. As concentration of filler increased abrasion resistance improved and achieved maximum value at filler load corresponding to 7 parts per hundred parts of rubber. Further increasing in filler loading resulted in gradual decrease of abrasion resistance

3.Out of three types of fillers tested: calcium carbonate, precipitated silica and fumed silica, the last two showed better abrasion resistance of gloves made of natural rubber based latex compounds filled with those fillers. Calcium carbonate being inert by its nature towards rubber molecules did not contribute to formation of strong bonds between filler particles and rubber chains, that led to poor abrasion performance. Both silica fillers being semi -reinforcing by their nature made it possible to form physical intermolecular bonds across rubber –filler interface.

4.It was found, that fumed silica having fine particles allowed to obtained better improvement of abrasion resistance if compared to more coarse particle size precipitated silica. Further improvement of abrasion resistance was achieved by using silane coupling agent together with fumed silica in natural rubber based latex compound. Optimization of concentration of silane coupling agent showed that the best performance was achieved at the 0.5 PHR level while maintaining fumed silica loading level at 7 PHR.

5. Determined mechanical performance of the industrial gloves made out of developed compound based on natural rubber latex filled with fumed silica and silane coupling agent showed that, not only abrasion performance, but cut resistance, punch resistance, tensile stress, Tabor abrasion, tear resistance, aging properties and blooming properties were improved,

However, it was observed that stiffness and laundry ability deteriorated. Grip property did not show any improvement and remained at the same level. In overall, using fumed silica combined with silane coupling agent improved the abrasion resistance of gloves by 6 times compared to abrasion of gloves made of the latex compound filled with calcium carbonate.

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10.APPENDICES

10.1. Appendix 1- EN Standards

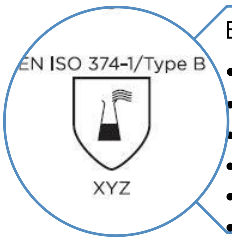
(Guide Glove, 2019) (Ansell, 2011)

EN420:2003

- **General requirements for protective gloves**
- Glove construction and design
- Innocuousness
- Cleaning Instructions
- Electrostatic Properties
- Water Vapour Transmission and Absorption
- Marking & Information
- Instructions for use
- Glove Sizing Chart

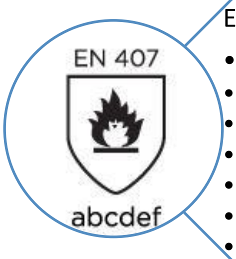
EN388: 2016

- **Mechanical Protection**
- Abrasion Resistance (cycles)
- Blade Cut Resistance (number)
- Tear Resistance (Newtons)
- Puncture Resistance (Newtons)
- ISO Cut Resistance (Newtons)
- EN Impact Protection



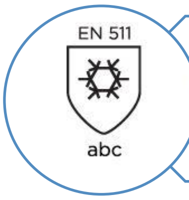
EN ISO 374: 2016

- **Chemical & Micro-Organism Protection**
- Penetration
- Permeation
- Degradation
- Virus protection ISO 16604
- Marking & Information



EN407: 2004

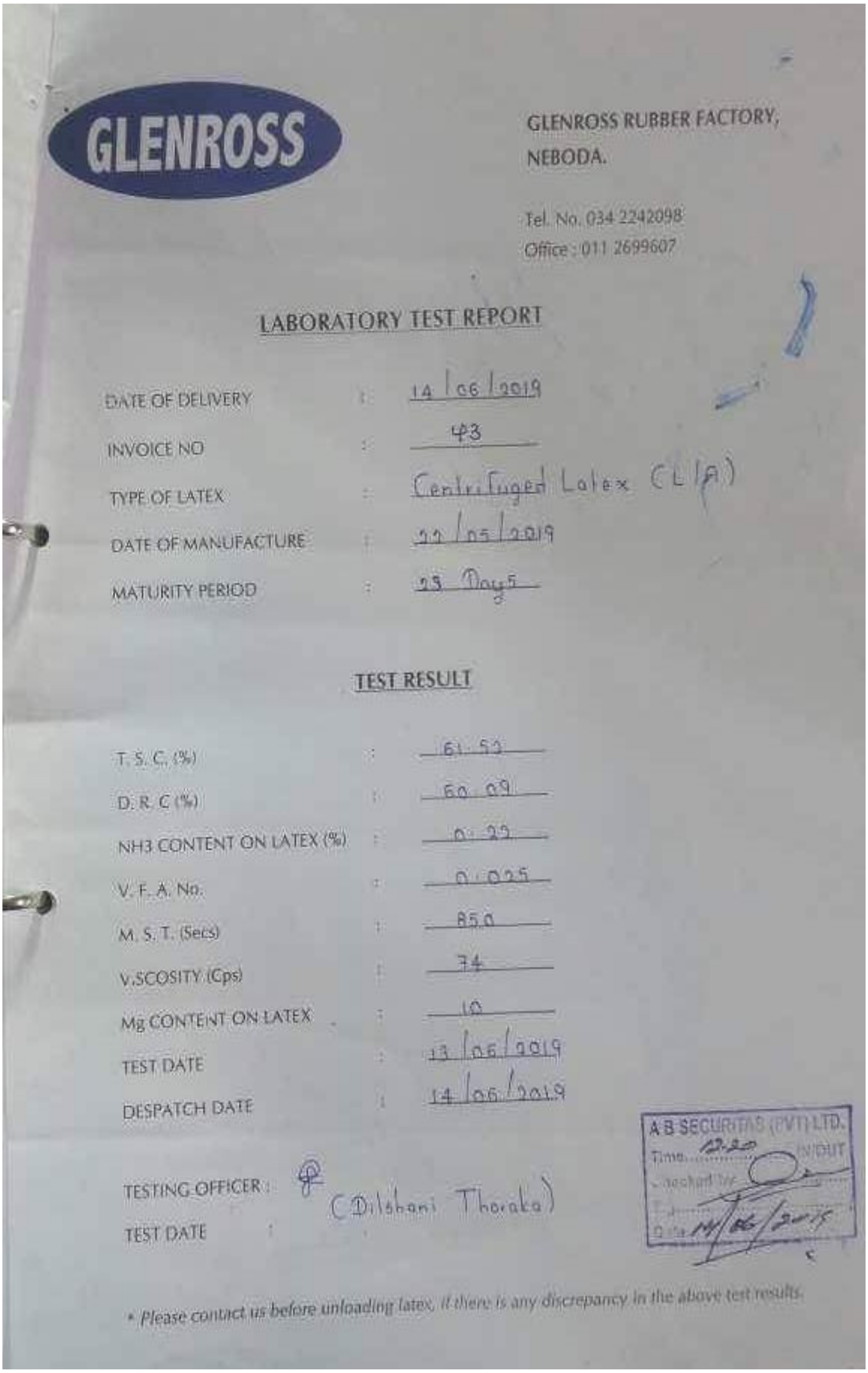
- **Thermal Protection**
- Resistance to Flammability (performance level 0–4)
- Contact Heat Resistance (performance level 0–4)
- Convective Heat Resistance (performance level 0–4)
- Radiant Heat Resistance (performance level 0–4)
- Resistance to Small Splashes of Molten Metal (performance level 0–4)
- Resistance to Large Quantities of Molten Metal (performance level 0–4)



EN511: 2006

- **Cold Protection**
- Resistance to Convective Cold (performance level 0–4)
- Resistance to Contact Cold (performance level 0–4)
- Penetration by Water (0 or 1)

10.2. Appendix 2 - Laboratory test report of centrifuged latex



GLENROSS

GLENROSS RUBBER FACTORY,
NEBODA.

Tel. No. 034 2242098
Office : 011 2699607

LABORATORY TEST REPORT

DATE OF DELIVERY : 14/06/2019
INVOICE NO : 43
TYPE OF LATEX : Centrifuged Latex (CL/A)
DATE OF MANUFACTURE : 22/05/2019
MATURITY PERIOD : 23 Days

TEST RESULT

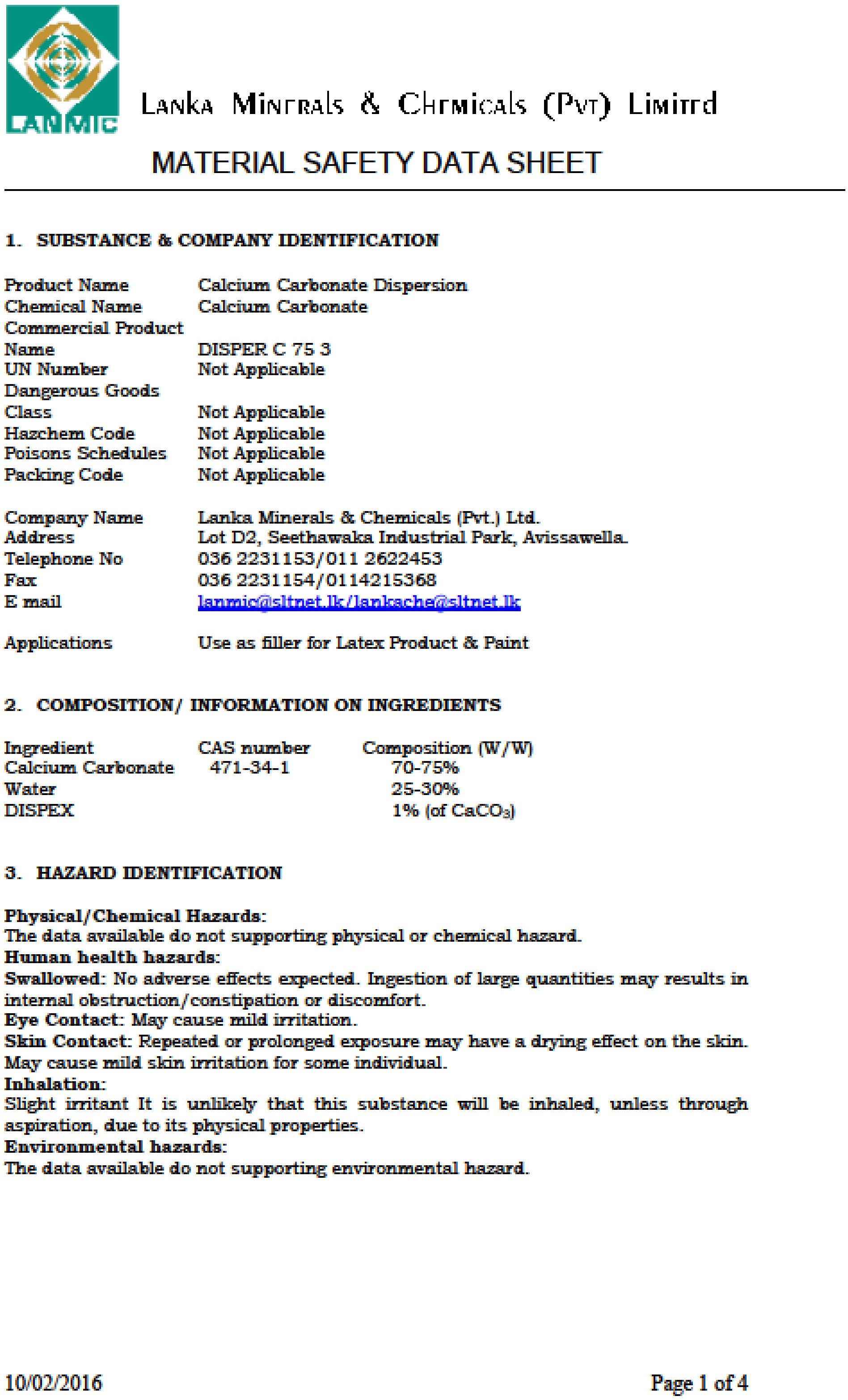
T. S. C. (%) : 61.52
D. R. C (%) : 60.09
NH3 CONTENT ON LATEX (%) : 0.22
V. F. A. No. : 0.025
M. S. T. (Secs) : 850
V.SCOSITY (Cps) : 74
Mg CONTENT ON LATEX : 10
TEST DATE : 13/06/2019
DESPATCH DATE : 14/06/2019

TESTING OFFICER : (Dilshani Tharaka)
TEST DATE :

A B SECURITAS (PVT) LTD.
Time 12.20 IN/OUT
Checked by
Date 14/06/2019

* Please contact us before unloading latex, if there is any discrepancy in the above test results.

10.3. Appendix 3 - MSDS of Calcium Carbonate



LANMIC

Lanka Minerals & Chemicals (Pvt) Limited

MATERIAL SAFETY DATA SHEET

1. SUBSTANCE & COMPANY IDENTIFICATION

Product Name	Calcium Carbonate Dispersion
Chemical Name	Calcium Carbonate
Commercial Product Name	DISPER C 75 3
UN Number	Not Applicable
Dangerous Goods Class	Not Applicable
Hazchem Code	Not Applicable
Poisons Schedules	Not Applicable
Packing Code	Not Applicable

Company Name	Lanka Minerals & Chemicals (Pvt.) Ltd.
Address	Lot D2, Seethawaka Industrial Park, Avissawella.
Telephone No	036 2231153/011 2622453
Fax	036 2231154/0114215368
E mail	lanmic@sltnet.lk/lankache@sltnet.lk

Applications	Use as filler for Latex Product & Paint

2. COMPOSITION/ INFORMATION ON INGREDIENTS

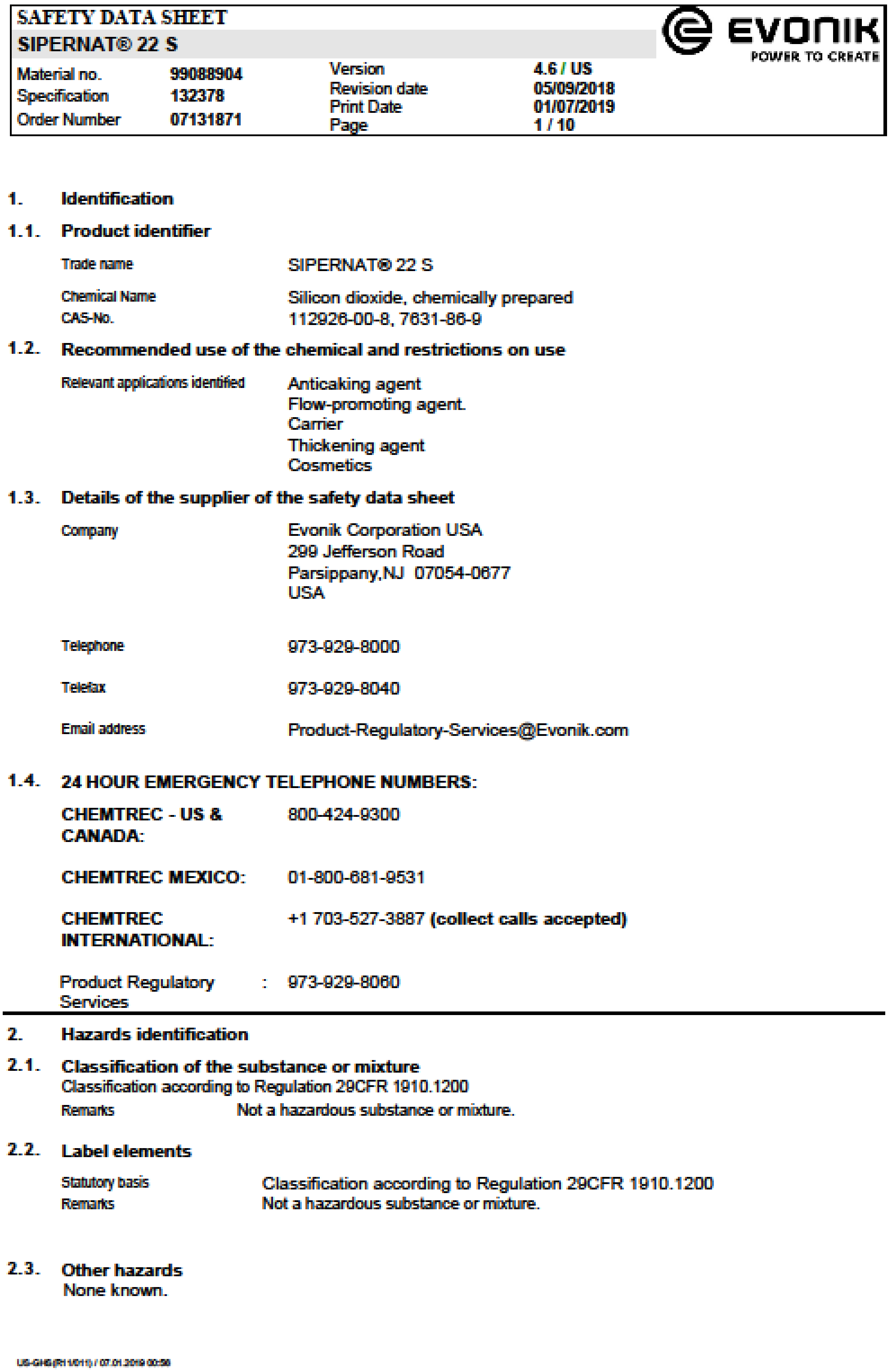
Ingredient	CAS number	Composition (W/W)
Calcium Carbonate	471-34-1	70-75%
Water		25-30%
DISPEX		1% (of $CaCO_3$)

3. HAZARD IDENTIFICATION

Physical/Chemical Hazards:
The data available do not supporting physical or chemical hazard.
Human health hazards:
Swallowed: No adverse effects expected. Ingestion of large quantities may results in internal obstruction/constipation or discomfort.
Eye Contact: May cause mild irritation.
Skin Contact: Repeated or prolonged exposure may have a drying effect on the skin. May cause mild skin irritation for some individual.
Inhalation:
Slight irritant It is unlikely that this substance will be inhaled, unless through aspiration, due to its physical properties.
Environmental hazards:
The data available do not supporting environmental hazard.

10/02/2016 Page 1 of 4

10.4. Appendix 4 – Precipitated Silica MSDS



SAFETY DATA SHEET

SIPERNAT® 22 S

Material no.	**99088904**	Version	**4.6 / US**
Specification	**132378**	Revision date	**05/09/2018**
Order Number	**07131871**	Print Date	**01/07/2019**
		Page	**1 / 10**

1. Identification

1.1. Product identifier

Trade name	SIPERNAT® 22 S
Chemical Name	Silicon dioxide, chemically prepared
CAS-No.	112926-00-8, 7631-86-9

1.2. Recommended use of the chemical and restrictions on use

Relevant applications identified	Anticaking agent Flow-promoting agent. Carrier Thickening agent Cosmetics

1.3. Details of the supplier of the safety data sheet

Company	Evonik Corporation USA 299 Jefferson Road Parsippany,NJ 07054-0677 USA
Telephone	973-929-8000
Telefax	973-929-8040
Email address	Product-Regulatory-Services@Evonik.com

1.4. 24 HOUR EMERGENCY TELEPHONE NUMBERS:

CHEMTREC - US & CANADA:	800-424-9300
CHEMTREC MEXICO:	01-800-681-9531
CHEMTREC INTERNATIONAL:	+1 703-527-3887 **(collect calls accepted)**
Product Regulatory Services :	973-929-8060

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2. Hazards identification

2.1. Classification of the substance or mixture

Classification according to Regulation 29CFR 1910.1200

Remarks Not a hazardous substance or mixture.

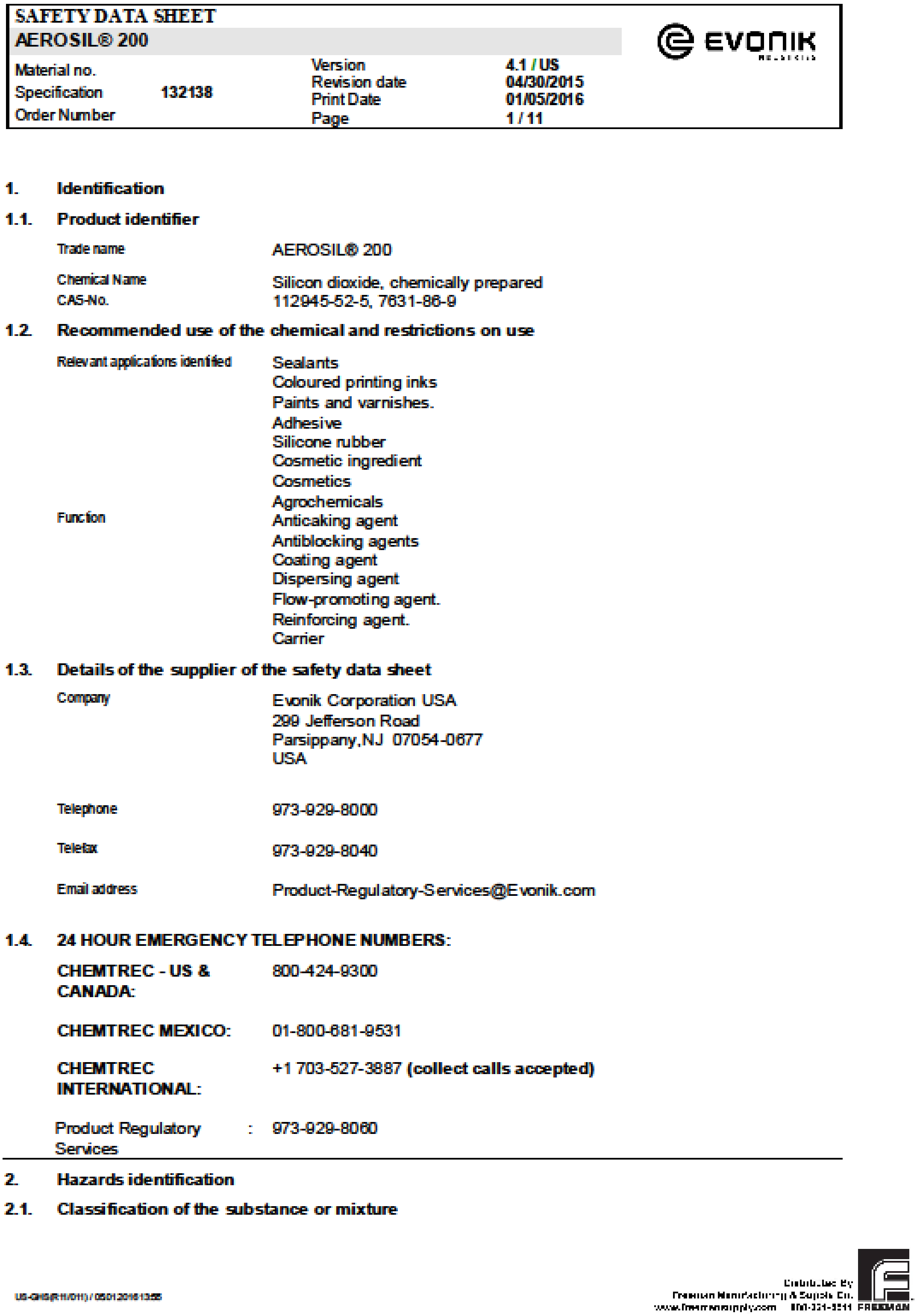
2.2. Label elements

Statutory basis	Classification according to Regulation 29CFR 1910.1200
Remarks	Not a hazardous substance or mixture.

2.3. Other hazards

None known.

10.5. Appendix 5 – Fumed Silica MSDS



SAFETY DATA SHEET

AEROSIL® 200

Material no.		Version	**4.1 / US**
Specification	**132138**	Revision date	**04/30/2015**
Order Number		Print Date	**01/05/2016**
		Page	**1 / 11**

1. Identification

1.1. Product identifier

Trade name	AEROSIL® 200
Chemical Name	Silicon dioxide, chemically prepared
CAS-No.	112945-52-5, 7631-86-9

1.2 Recommended use of the chemical and restrictions on use

Relevant applications identified	Sealants Coloured printing inks Paints and varnishes. Adhesive Silicone rubber Cosmetic ingredient Cosmetics Agrochemicals
Function	Anticaking agent Antiblocking agents Coating agent Dispersing agent Flow-promoting agent. Reinforcing agent. Carrier

1.3. Details of the supplier of the safety data sheet

Company

Evonik Corporation USA
299 Jefferson Road
Parsippany,NJ 07054-0677
USA

Telephone	973-929-8000
Telefax	973-929-8040
Email address	Product-Regulatory-Services@Evonik.com

1.4. 24 HOUR EMERGENCY TELEPHONE NUMBERS:

CHEMTREC - US & CANADA:	800-424-9300
CHEMTREC MEXICO:	01-800-681-9531
CHEMTREC INTERNATIONAL:	+1 703-527-3887 **(collect calls accepted)**
Product Regulatory Services :	973-929-8060

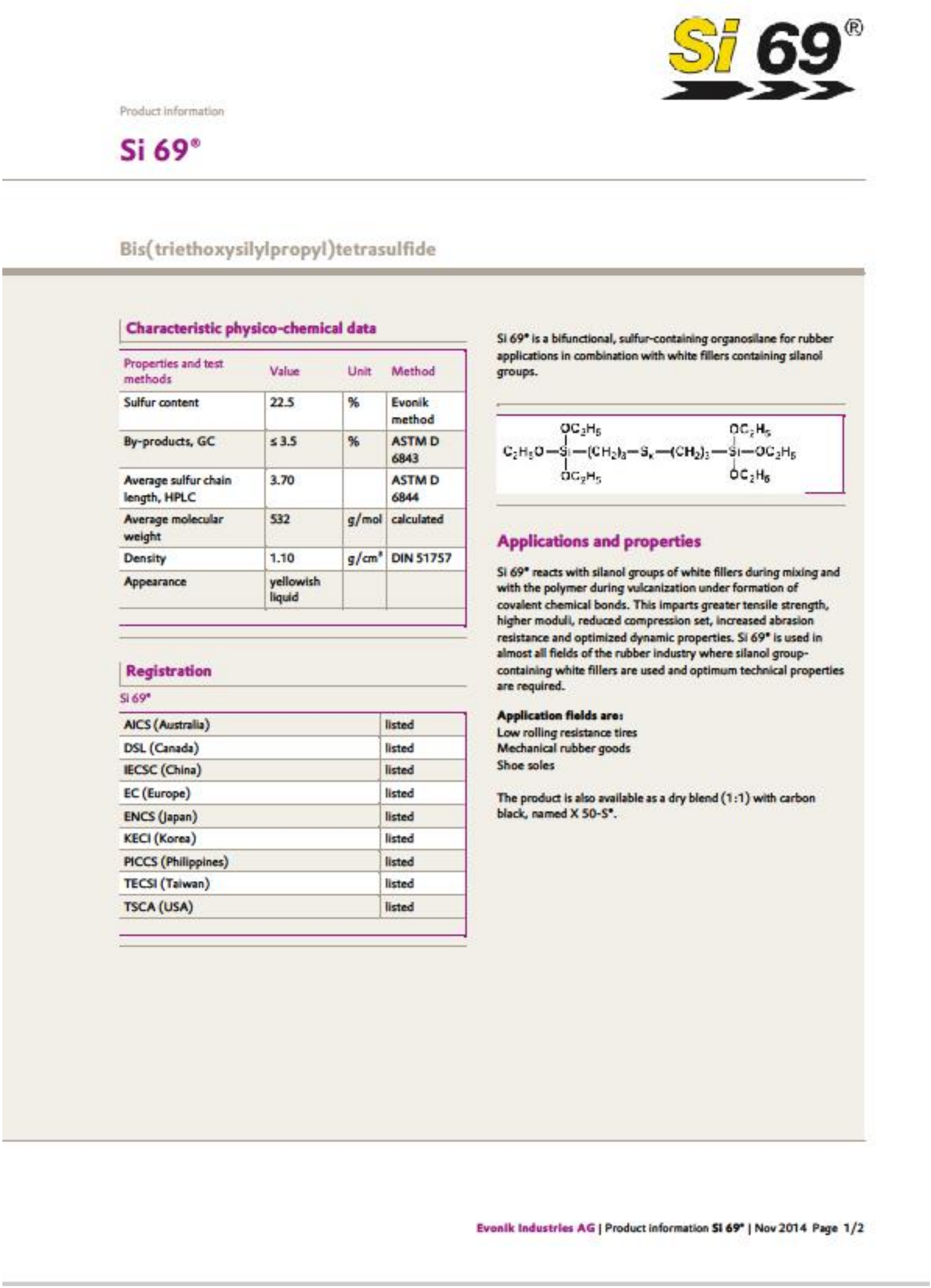
2. Hazards identification

2.1. Classification of the substance or mixture

US-GHS(R11/011) / 050120161355

Distributed By
Freeman Manufacturing & Supply Co.
www.freemansupply.com
FREEMAN

10.6. Appendix 6 – Silane Coupling agent MSDS



Product information

Si 69®

Bis(triethoxysilylpropyl)tetrasulfide

Characteristic physico-chemical data

Properties and test methods	Value	Unit	Method
Sulfur content	22.5	%	Evonik method
By-products, GC	≤ 3.5	%	ASTM D 6843
Average sulfur chain length, HPLC	3.70		ASTM D 6844
Average molecular weight	532	g/mol	calculated
Density	1.10	g/cm^3	DIN 51757
Appearance	yellowish liquid		

Registration

Si 69®

AICS (Australia)	listed
DSL (Canada)	listed
IECSC (China)	listed
EC (Europe)	listed
ENCS (Japan)	listed
KECI (Korea)	listed
PICCS (Philippines)	listed
TECSI (Taiwan)	listed
TSCA (USA)	listed

Si 69® is a bifunctional, sulfur-containing organosilane for rubber applications in combination with white fillers containing silanol groups.

$$C_2H_5O-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-(CH_2)_3-S_x-(CH_2)_3-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-OC_2H_5$$

Applications and properties

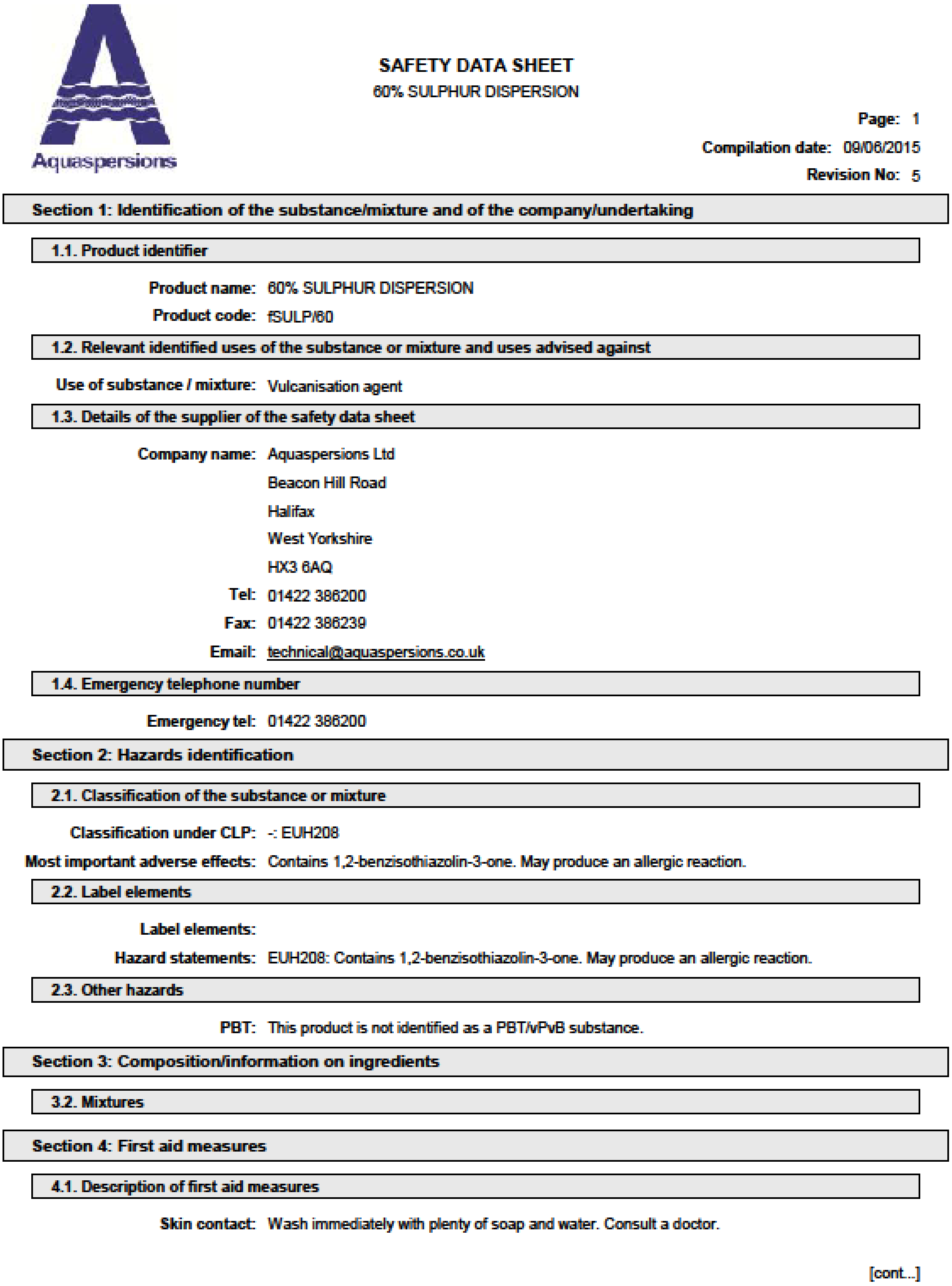
Si 69® reacts with silanol groups of white fillers during mixing and with the polymer during vulcanization under formation of covalent chemical bonds. This imparts greater tensile strength, higher moduli, reduced compression set, increased abrasion resistance and optimized dynamic properties. Si 69® is used in almost all fields of the rubber industry where silanol group-containing white fillers are used and optimum technical properties are required.

Application fields are:
Low rolling resistance tires
Mechanical rubber goods
Shoe soles

The product is also available as a dry blend (1:1) with carbon black, named X 50-S®.

Evonik Industries AG | Product information **Si 69®** | Nov 2014 Page 1/2

10.7. Appendix 7 – Sulfur Dispersion MSDS



Aquaspersions

SAFETY DATA SHEET

60% SULPHUR DISPERSION

Page: 1

Compilation date: 09/06/2015

Revision No: 5

Section 1: Identification of the substance/mixture and of the company/undertaking

1.1. Product identifier

Product name: 60% SULPHUR DISPERSION

Product code: fSULP/60

1.2. Relevant identified uses of the substance or mixture and uses advised against

Use of substance / mixture: Vulcanisation agent

1.3. Details of the supplier of the safety data sheet

Company name: Aquaspersions Ltd
Beacon Hill Road
Halifax
West Yorkshire
HX3 6AQ

Tel: 01422 386200

Fax: 01422 386239

Email: technical@aquaspersions.co.uk

1.4. Emergency telephone number

Emergency tel: 01422 386200

Section 2: Hazards identification

2.1. Classification of the substance or mixture

Classification under CLP: -: EUH208

Most important adverse effects: Contains 1,2-benzisothiazolin-3-one. May produce an allergic reaction.

2.2. Label elements

Label elements:

Hazard statements: EUH208: Contains 1,2-benzisothiazolin-3-one. May produce an allergic reaction.

2.3. Other hazards

PBT: This product is not identified as a PBT/vPvB substance.

Section 3: Composition/information on ingredients

3.2. Mixtures

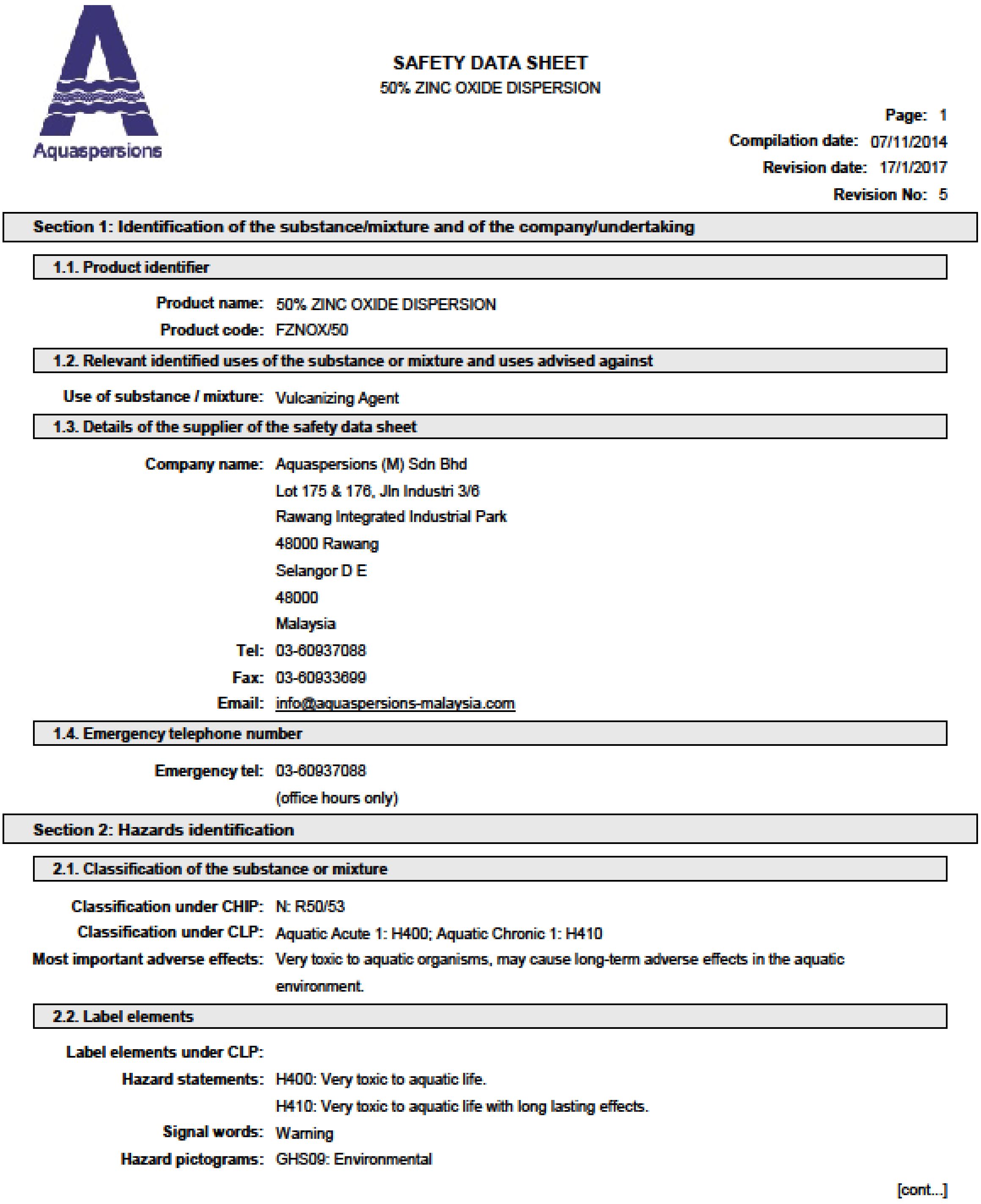
Section 4: First aid measures

4.1. Description of first aid measures

Skin contact: Wash immediately with plenty of soap and water. Consult a doctor.

[cont...]

10.8. Appendix 8 – Zinc Oxide Dispersion MSDS



Aquaspersions

SAFETY DATA SHEET

50% ZINC OXIDE DISPERSION

Page: 1
Compilation date: 07/11/2014
Revision date: 17/1/2017
Revision No: 5

Section 1: Identification of the substance/mixture and of the company/undertaking

1.1. Product identifier

Product name: 50% ZINC OXIDE DISPERSION
Product code: FZNOX/50

1.2. Relevant identified uses of the substance or mixture and uses advised against

Use of substance / mixture: Vulcanizing Agent

1.3. Details of the supplier of the safety data sheet

Company name: Aquaspersions (M) Sdn Bhd
Lot 175 & 176, Jln Industri 3/6
Rawang Integrated Industrial Park
48000 Rawang
Selangor D E
48000
Malaysia
Tel: 03-60937088
Fax: 03-60933699
Email: info@aquaspersions-malaysia.com

1.4. Emergency telephone number

Emergency tel: 03-60937088
(office hours only)

Section 2: Hazards identification

2.1. Classification of the substance or mixture

Classification under CHIP: N: R50/53
Classification under CLP: Aquatic Acute 1: H400; Aquatic Chronic 1: H410
Most important adverse effects: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

2.2. Label elements

Label elements under CLP:
Hazard statements: H400: Very toxic to aquatic life.
H410: Very toxic to aquatic life with long lasting effects.
Signal words: Warning
Hazard pictograms: GHS09: Environmental

[cont...]