

**INVESTIGATION OF THE EFFECT OF MOLD
RELEASING AGENT AND RESIDUAL CALCIUM
NITRATE/CALCIUM ION OF NITRILE HIGHER MIL
GLOVES TO WET LOOK DEFECT**

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of Science in Polymer Technology

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DECLARATION

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ABSTRACT

Two types of latex are used in disposable gloves manufacturing as natural latex and synthetic latex. Calcium nitrate (calcium ion) is used as the coagulant and calcium carbonate or calcium stearate is used as the former releasing agent.

In pre leaching of natural latex gloves, protein removal also required other than the calcium nitrate removal and post leaching is necessary to further removal of protein. Effectiveness of leaching depends mainly on - three factors as leaching time, leaching tank condition and leaching temperature. In natural latex gloves, it can be maintained leaching takes place at a higher temperature since natural rubber has a high crystalline temperature. But in synthetic latex gloves manufacturing, it cannot be kept at the leaching tank temperature at higher temperatures since the glove becomes hard since its crystalline temperature is low. If the glove film has high thickness, leaching is difficult. Limitation of water supply and high wastewater treatment costs are the main issues with leaching.

Chlorination is used to modify the disposable glove surface by reducing the tackiness which is a characteristic of rubber. Chlorination reduces the friction between the rubber surface and the other surface which come into contact. There are two types of chlorination as online chlorination and offline chlorination. Online chlorination is done by immersing the glove into a chlorine water tank before removing the glove from the former. At online chlorination, the inner surface of the glove gets smoother. If smoothness of the outside surface also requires, offline chlorination is done as a batch process in chlorinators (a machine like a washing machine). Other than that, chlorine water solution can convert calcium carbonate/ calcium stearate which is used as the former releasing agent to calcium salts. There are some disposable gloves which the chlorination is in complete. Chlorination is used to reduce the tackiness resulted from this incomplete chlorination.

Calcium ion can absorb moisture from the surrounding. If calcium ion remains on the latex glove surface, it gives a wet look by absorbing the surrounding moisture. In the industry, it is called "Oil marks". The degree of wet look depends on calcium ion concentration and surrounding moisture content. If the glove surface contains a

moisture absorbing material like calcium carbonate or corn starch, wet look is not visible even if the glove surface has a significant amount of calcium ions.

DEDICATION

This thesis is dedicated to gloves stripping girls who get burnt their hands to protect someone else hand.

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LIST OF ABBREVIATIONS

CAN	- Acrylonitrile
HCl	- Hydrochloric Acid
BT	- Break through time
PPM	- Parts per million
PPT	-Parts per thousand
TSC	- Total Solid Content
FTIR	- Fourier-transform infrared
GC	- Gas chromatography
EDTA	- Ethylenediaminetetraacetic acid
EBT	- Eriochrome Black T

**1 CHAPTER 1:
RESEACH INTRODUCTION**

1.1 Background

Disposable gloves manufacturing is a high volume, low-profit margin business. Both natural latex and synthetic latex are used for disposable gloves manufacturing. Due to allergy concerns, the demand for natural latex gloves is getting decreased while the demand for synthetic latex gloves increases. But if high elasticity properties are required, natural latex is the only option. Synthetic latex gloves have a good demand when high chemical resistance and high puncher resistance is required. The unit “mil” is used in the glove industry to measure the glove thickness. To survive in this business, manufacturing cost reduction is essential.

Most of the disposable glove consumers are from European countries and north American countries. Also in contrast to Asian countries they have strict quality control focus. Even regulation bodies like FDA, has a concern on consumer protection and they do not allow low quality goods to come in to the country even the end user is willing to use them. Glove quality is assured based on the acceptance quality level (AQL)

Wet look is a big industrial issue which associates with higher thickness gloves and when the glove has high chemical resistance properties, this defect is severe. Since wet look area has an oil like surface, wet look is called as “oil marks” in industry. If one wet look glove is found in the sample inspection, entire batch would be returned back for rework. . This reworking incurs additional considerable amount of costs for the manufacturing cycle.. If the wet look area is small that will be a cosmetic defect and if the wet look are is considerably large, it is a major defect since it creates glove donning issues. Preliminary industrial observation is that the wet look is due to insufficient leaching. But in leaching, too much leaching is costly . Oil mark is not visible just after stripping of the glove and it takes time. So mass transfer from the rubber phase to the surface is obvious. If a glove has wet look defect, it contains more extractable substance and it will violate or compromise some compliances in FDA.

1.1.1 Problem statement

When chemical resistance is required, high acrylonitrile polymers are used to produce high mil (thickness) gloves. Wet look/oil mark is the glove surface has an oil like substance which customers do not accept. This cannot be observed just after stripping and with time this can be observed. Because of this, glove donning also difficult.

1.1.2 Problem categorization

“Wet-look” defect has no acceptance level and if it is visible or above 25 cm visible inspection level, it is considered as a wet look glove. AQL based sample inspection states that if one wet look glove was found, hold the entire for re-work (Accept no defect). Reworking is done through cyclone drying and it cost is around 2 USD per 1000 glove pieces.



Figure 1.1-1 Gloves inspection

There are two types of wet look observations are common in the industry as below

1. Without the offline chlorination, wet look can be observed at cuff area of the glove. Especially, this can be observed in online chlorinated calcium stearate mold releasing agent styles (After offline chlorination this can be observed in calcium carbonate mold releasing agent styles also). **TYPE A**

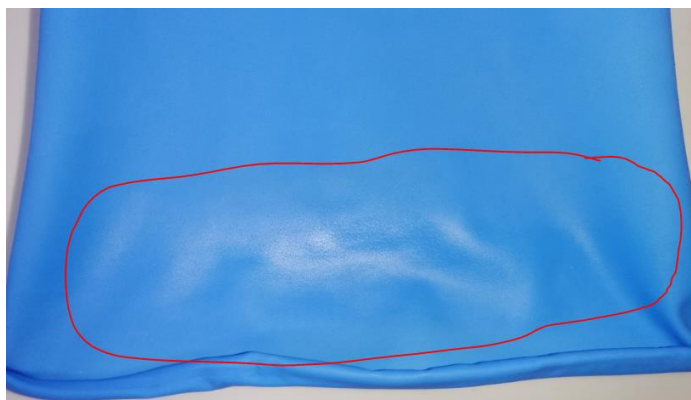


Figure 1.1-2 Type A wet look

2. Without the offline chlorination, wet look cannot be observed and a few hours after offline chlorination, wet look can be observed only at just below the bead area. **TYPE B**



Figure 1.1-3 Type B wet look

1.2 Research Objectives

The aim of the study was to find out the relationship between leaching, chlorination & mold releasing agent for the wet look defect of high thickness synthetic latex

gloves, high acrylonitrile content(41%) disposable gloves. So objectives of the study are

1. Finding the minimum residual calcium nitrate concentration after leaching that can be migrated to the surface
2. Finding the relationship of degree of chlorination vs chemical permeability to describe the calcium carbonate mold releasing agent conversion to calcium salt

1.3 Rationale of the Study

Most of the disposable gloves researches have been done to study the protein effect on allergies and its mitigation methods. But those studies are limited to and more focused on pre-leaching behaviours. In some studies, it has been found that calcium ion cause wet look defects. But they had been focused to reduce that by removing calcium ions following some after processes. In the industry, there are two types of wet look defect and very limited researches had been identified and discussed in the capacity of finding the root causes. This study focuses on the effect on mold releasing agent on wet look defect which will be able to make a significant contribution to fill a gap in the research area.

1.4 Significance of the Research

Disposable glove manufacturing industry attributes to a big significantly high portion of the polymer industry. Since it has been explained the manufacturing process in technically here, newcomers to the glove industry can have a sound knowledge of the disposable gloves manufacturing process. As explained earlier, disposable gloves manufacturing is a low-profit margin high volume business. By referring this study, industrial people can find their optimum leaching level and gaps in their processing conditions. This research can be used to industries that are looking for new mold releasing agents development since reaction with acid is a design factor. As well as this will be a referring material for future researches in the disposable glove manufacturing industry.

1.5 Chapter Organisation

In chapter one, it has been described why this topic was selected and what benefits to the society by solving this problem.

In the second chapter it has been described the related studies which have been done so far.

In the third chapter, it describes identification of the problem, the testing which has been done to check the hypothesis and the way those testing were conducted.

In the fourth chapter, it has been mentioned results of the testing which have been done in chapter three along with results justifications and elaborations.

In the final chapter, chapter five, the conclusion of this study has been stated.

**2 CHAPTER 2:
LITERATURE REVIEW**

2.1 Gloves

As a personal protective equipment (PPE), gloves are used to protect hand or part of the hand against hazards. These hazards can be chemical, mechanical, physical, electrical, micro biological and environmental (heat/cold). Gloves can be divided into two main categories as supported and unsupported. Unsupported gloves can be categorized as disposable and household. Supported gloves can be further categorized as industrial gloves, sport gloves and winter gloves. (Fontaine, 2019; Group, 2019; KCL, 2014)

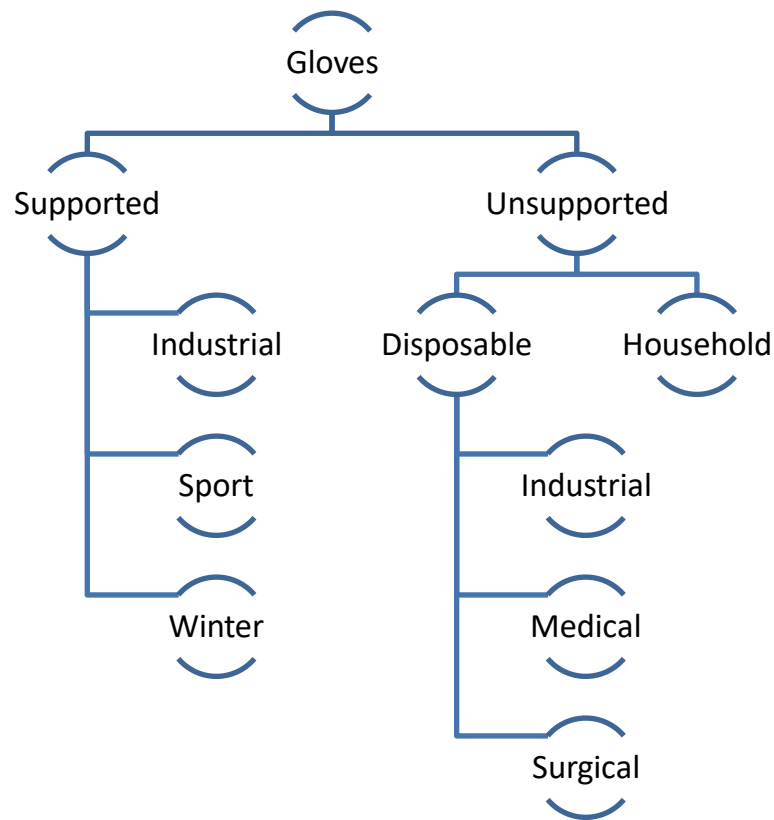


Figure 2.1-1 Gloves categorization

Supported gloves need a fabric liner and polymer coating is done over the fabric liner. Fabric liner determine the glove properties like cut resistance, abrasion resistance, tear resistance, puncher resistance, sweat absorption and comfort hand feelings while polymer coating determines the abrasion resistance, shock absorption, chemical resistance, electrical resistance, heat transfer and the grip. Nylon, polyester, glass, steel, cotton, Kevlar are main yarn are used to manufacture the fabric liner.

Natural latex, synthetic latex, neoprene, PVC and silicone are main polymers which are used to make the polymer coating over the fabric coat.

Unsupported household gloves are used for kitchen applications and gardening applications. Cotton flock is used when sweat absorption is required and house hold gloves outer surface has patterns in order to enhance the grip. Since polymer weight of the household gloves are high compound cost reduction is focused in household gloves manufacturing. Disposable gloves are single use gloves twenty minutes is the typical wearing time. Disposable industrial gloves are used in material handling and industrial examination process. Medical gloves is for the medical staff to examine patients. Surgical gloves is for the operation theatre applications. Natural latex and acrylonitrile butadiene are main polymers used for unsupported gloves manufacturing. Since good elasticity in natural latex gloves, it fits to the hand well. (M-Predolich, 2019; Akabane, 2016; Pro, 2019)

2.2 Disposable Gloves

Worldwide disposable gloves annual manufacturing is 300 billion pieces and Malaysia claims 63% of the total production. (Star-The, 2019)

Polymer wise disposable gloves manufacturing breakup as below

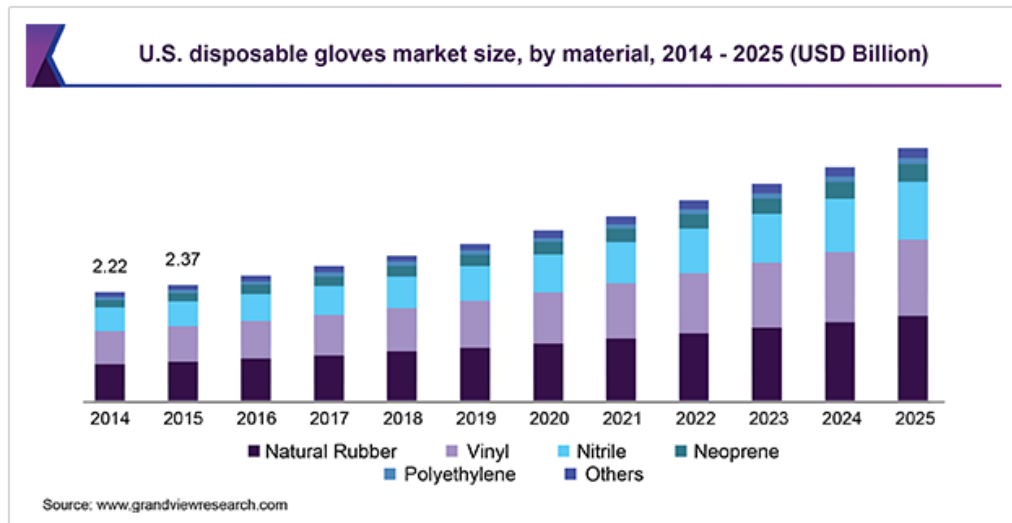


Figure 2.2-1 Disposable gloves market size

Source - (Research, 2017)

Since disposable gloves are single use and high consuming gloves, cost should be low. Below are the typical cost reduction options in the disposable glove industry.

- Replace high cost raw materials with low cost raw materials
- Increase production output to reduce fixed overhead
- Switch for low cost utility options
- Introduce automation to reduce labour cost
- Reduce glove weight to its optimum level
- Optimize the water usage for washing and leaching purposes
- Eliminate heat losses
- Select AQL based on the application (Avoid unwanted tight inspections)

(Akabane, 2016)

2.2.1 Compound ingredients

Compound ingredients selection depend on the glove properties and customer requirement. As it described in the introduction and 2.1, natural latex has good elastic properties which can give perfect glove fitting to the hand and also economical than synthetic latex. But natural latex has low chemical resistance associated with allergy concerns, natural latex gloves demand does not significantly increase. By using synthetic latex, various beneficial properties can be achieved such as chemical resistance, puncher resistance, thermal stability and good aging properties. Typical compound ingredients as below.

- Latex
- Dispersion
- ph. Modifiers
- Pigment
- Wax
- Surfactants
- Biocide
- Water (De-ionized water)

The dispersion can break up further

- Crosslinking agents
- Accelerator
- Activators
- Antioxidant
- Dispersion agents
- pH Modifiers
- Pigment
- Water (De-ionized water)

(Francis, 1987; M, 2019)

2.2.1.1 Latex

Latex can be divided in to two categories as natural latex and synthetic latex. Natural latex is taken by tapping from Brasiliensis tree. Raw latex contains around 70% of non rubbers and water. Latex can be centrifuged and increased its rubber content up to 60% to avoid high transportation cost and cater high rubber content requirements. Natural latex quality parameters are Viscosity, total solid content (TSC), mechanical stability time (MST), dry rubber content (DRC), Alkalinity (Ammonia Content), KOH number and Volatile fatty acid number (VFA number), Toluene swelling index (TSI),

Synthetic latex is produced as a by-product of polymerization process of petroleum products. Typically maximum polymer content of synthetic latex is 41% and stabilizers are used for the stabilization. Unlike in natural latex, total solid content (TSC) and pH are only quality controlling parameters. (Anon., 1997; NG-K.P, 1995)

2.2.1.1.1 Carboxylated acrylonitrile butadiene latex

This is the most widely used synthetic latex in the gloves industry. Other than the acrylonitrile and butadiene, a small amount carboxylic group is present. When carboxylic group is introduced, unsaturation decreases and it facilitate to create metal ion bonds.

(Liyanaarachchi, 2008)

2.2.1.2 Dispersion

The dispersion ingredients to make crosslinks between latex particle. In glove industry sulphur is used as the crosslinking agent. Sulphur is not very chemically active. So it need accelerators to expedite the crosslinking formation. Sulphur to accelerator ratio determine the cross link structure. If sulphur is too high long sulphur bond are formed and tensile strength and elasticity of final glove is high while high accelerator content will result short sulphur bonds and tensile strength and elasticity of final glove is low. Selection of accelerators depend on the rate of curing. Typically more than one accelerator is used to for a synergistic effect.

Table 2.2-1 Accelerator selection

Source - (Limited, 2002)

<u>Accelerators</u>	<u>Chemical Group</u>	<u>Vulcanization Speed</u>
BA, HMT	Aldehyde Amine	Slow
DPG, DOTG	Guanidine	Slow
MBT, MBTS, ZMBT	Thiazole	Semi Ultra fast
ZBDP	Thiophosphate	Ultra fast
CBS, TBBS, MBS, DCBS	Sulfenamides	Fast-Delayed action
ETU, DPTU, DBTU	Thiourea	Ultra fast
TMTM, TMTD, DPTT, TBzTD	Thiuram	Ultra fast
ZDMC, ZDEC, ZDBC, ZBEC	Dithiocarbamate	Ultra fast
ZIX	Xanthates	Ultra fast

Activators are used to activate the accelerators. In industry zinc oxide is used as the activator. Zinc oxide has only activator function in natural latex. Since carboxylate synthetic latex is used for synthetic latex gloves, zinc oxide creates ionic bonds also. This zinc oxide ionization is high at high ph. If KOH/NaOH are used ,in order to increase the pH, at times ammonia solution is used. this ionization is high (six ammonia moles are required to ionize one zinc oxide mole. But one KOH/NaOH mole can ionize one zinc mole). If too many ionic bonds are there, the glove ends up with a hard/plastic feeling and that reacts with sweat while wearing. Antioxidants are required to protect gloves from environmental degradation . typically phenol base antioxidants are used since decolourisation is a selection criteria. natural latex unsaturation is higher than the synthetic latex, natural latex need more antioxidants. Dispersion agents are used to ensure the homogenize dispersion mixing and prevent

settling. Typically Naphthalenesulfonic acid-formaldehyde-polycondensate is used as the dispersion agent in glove industry. To ensure the basis pH of the final dispersion, potassium hydroxide is added to the dispersion. Final glove colour is also a quality parameter as a pigment titanium dioxide is added to keep the dispersion solution white. This titanium dioxide will give a bright colour to the final glove. (Lanka, 2003; Team-Evonik, 2019)

2.2.1.3 pH Modifiers

pH also has a big contribution to the glove film thickness. Latex is stable at high pH. So stability is difficult if the pH is high. High pH has a low thickness than the low pH. The typical range for the pH for synthetic latex is 9-10 and for natural latex, it is 10-11. Ammonia and KOH are used to increase the pH. Ammonia evaporates with time. So pH stability is less with ammonia. But there are limitations on using KOH to increase pH. Since KOH needs to be diluted prior to adding. If final compound TSC requirement is high, it cannot be used with much water to dilute the KOH. Typically for better performance, both KOH and ammonia is used for the formulation. (Francis, 1987)

2.2.1.4 Pigments

Most of the pigments are volatile organic components. Pigment selection basically depends on the cost of the pigment and compliance to standards like REACH compliance. (M, 2019)

2.2.1.5 Wax

Wax is not compatible with latex, hence after curing excessive wax migrates to the glove surface and acts as a barrier in order to prevent discolorations/degradation from gasses. It also gives a shiny look to the glove surface (Francis, 1987)

2.2.1.6 Surfactants

Surfactants (Surface active agents) 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. There are four main types of surfactants as non-ionic, anionic, cationic, amphoteric. Non-ionic surfactants are long chain alcohols, Anionic surfactants contain anionic functional groups at their head, a

positively charged head is present in cationic surfactants and amphoteric surfactants has both cationic and anionic centers attached to the same molecule. (Hirsch, 2015; LE, 2013)

2.2.1.7 Biocides

Typically microbial growth happens in the compound. Natural latex compound has a high pH. So the rate of microbial growth is less in natural latex compound. But it cannot be maintained at a higher pH. For synthetic latex gloves, it is better to add small amount of biocide for reduce the rate of microbial growth. (Sanitize, 2019)

2.2.1.8 Water

Latex gets destabilized at divalent ions. Calcium and magnesium ion are contained in normal hard water. If normal water is used there will be coagulum in the compound tank. Ion exchange resin is used to produce de-ionized water and de-ionized water is used for the compounding. (Riyajan, 2010)

2.2.2 Coagulant Ingredients

Typical coagulant ingredients are as below

- Coagulants
- Mold releasing agents
- Wetting agents
- Antifoaming agents

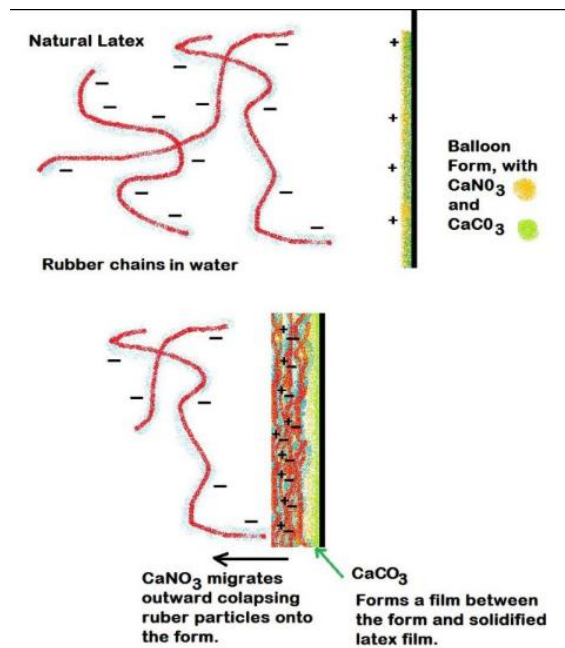


Figure 2.2-2 The coagulation process

Source - (Makeballoons, 2010)

2.2.2.1 Coagulants

A divalent ion is used as the coagulant. Typical coagulants are calcium nitrate and calcium chloride in the glove industry. Glove thickness depends on the coagulant strength and latex dipping TSC. So its effect is minimal. As an example, if glove thickness is 1 mm, it can be attained at 30% calcium nitrate strength and 41% latex TSC. Also, the same thickness can be taken at 29% calcium nitrate strength and 41.5 % latex TSC. Typically 2% coagulant change effects on 1% TSC change. In glove manufacturing, actually gelation happens. In gelation, it creates an even network structure. So it cannot be taken the same 1mm even glove film at 22% calcium nitrate strength and 44 % latex TSC. So it has limitations on changes. If calcium nitrate is the coagulant, the coagulant tank has pH around 4-7. This acidic condition also helps to reduce latex pH and make an even glove film. This is good to make high thickness films. If coagulant is calcium chloride it has the coagulant tank pH at 8-9 range. So not good to make high thickness films. Due to the corrosion effect and impurities, calcium chloride is not in use widely. (Limited, 2002; Than.L, n.d.)

2.2.2.1.1 Calcium Nitrate

Calcium nitrate is an inorganic compound with the formula $\text{Ca}(\text{NO}_3)_2$. This is a salt and absorb moisture from the surround to form tetra hydrate. purity of this coagulant is around 75%. Calcium nitrate is produced from the reaction between calcium carbonate and nitric acid. (group-Aravind-Mafatlal, 2010)



Figure 2.2-3 Calcium nitrate

2.2.2.2 Mold releasing agents

As explained above, there are two main types of mold releasing agents as calcium carbonate and calcium stearate. In industry, the selection depends on the cost and the final glove surface requirements. Calcium carbonate is cheaper than calcium stearate. By referring below surface options, anyone can identify the mold releasing agent selection. In glove stripping from the former, the outside surface become the inside surface, that is the hand donning side.



Figure 2.2-4 Gloves stripping

Table 2.2-2 Mold releasing agent selection

Wearing side	Outside surface	Mold Releasing agent	Online chlorination	Donning powder	Offline chlorination
Powder	Powder	Cal. carbonate	NA	Required	NA
Powder	Powder free	Cal. Stearate	NA	Required	NA
Powder free	Powder	Cal. carbonate	Required	NA	NA
Powder free	Powder free	Cal. Stearate	Required	NA	Optional
Powder free	Powder free	Cal. carbonate	Required	NA	Required

The mold releasing agent had two main functions. The first one is the glove film is made on the mold releasing agent surface. Under insufficient mold releasing agent, glove film will be sticky to the former and it creates stripping difficulties along with uneven glove film surface. The mold releasing agent is the carrier for the coagulant. So that is divalent ions are trapped between mold releasing agents (group-Aravind-Mafatlal, 2010)

2.2.2.2.1 Calcium carbonate

Calcium carbonate chemical compound has formula CaCO_3 . It is a common substance found in rocks as the minerals calcite and aragonite. (most notably as limestone, which is a type of sedimentary rock consisting mainly of calcite) and is the main component of pearls and the shells of marine organisms, snails, and eggs. For the glove manufacturing process, calcium carbonate should be in the powder form. (Lanka, 2003)



Figure 2.2-5 Calcium carbonate

2.2.2.2.2 Calcium stearate

Calcium stearate is a carboxylate of calcium, it has a yellowish white colour and classified as a calcium soap. It is a component of some lubricants, surfactants, as well as many food articles.. Calcium stearate is usually produced by heating stearic acid and calcium oxide. (Makeballoons, 2010)

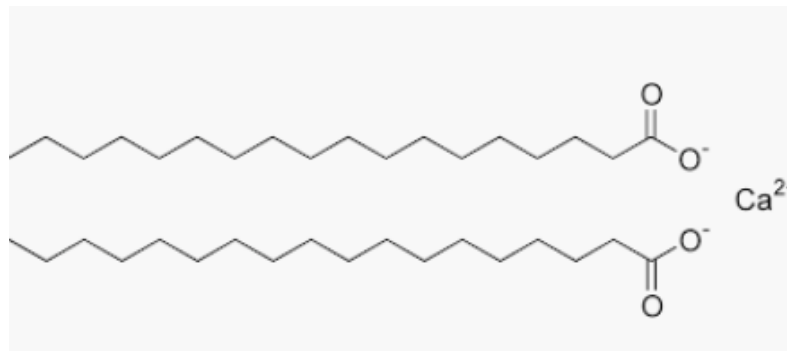


Figure 2.2-6 Calcium stearate

2.2.2.3 Wetting agent

The wetting agent is a non-ionic surfactant. Since one part of the agent is compatible with the ceramic former and the other part is compatible with mold releasing agent, it is the linking media to ceramic former and mold releasing agent. Under the insufficient wetting agent, the glove film will have uneven surface defect. Since the wetting agent is more compatible with the calcium stearate than the calcium carbonate, the calcium stearate concentration requirement is lesser than the calcium carbonate concentration requirement for the mold releasing. (Makeballoons, 2010)

2.2.2.4 Antifoaming agent

This is a silicon-based chemical. Two main functions are expected by adding this. Since the formers are moving in the coagulant tank bubbles formation is there and these bubbles create visible hole defects on the glove surface. Anti-webbing agents will break that bubbles (First function). Because of the surface tension, web formation happens between fingers and it results in visible holes between fingers. This anti-webbing chemical can break the web (Second function). Since this is hydrophobic, it comes to the coagulant tank surface. formers will carry them away. time to time feeding is required. If the dosage of anti-webbing is high, former wetting will be compromised in order to create uneven glove film. 200 grams per 20000 glove pieces is the industrial typical usage. (Makeballoons, 2010)

2.3 Disposable gloves manufacturing process

Disposable gloves manufacturing is a continuous process and it has two sub process as below

- Online dipping process
- Offline chlorination process

2.3.1 Online dipping process

Online dipping process consist below sub operations

2.3.1.1 Former cleaning with Acid

Here nitric acid is used and the main purpose is to oxidize organic components. Also, it removes calcium carbonate mold releasing agent or converts calcium stearate mold releasing agent into stearic acid in order to remove in the Alkali tank. Here a small amount of surfactant is also used to improve the cleaning efficiency. The typical nitric acid concentration is 2 w/w % and around 55 Celsius temperature is maintained. Acid level should be maintained higher than the coagulant level. (Bhd, 2019)

2.3.1.2 Former brushing

Former brushing is done with plastic brush rollers and it helps in the cleaning process

2.3.1.3 Alkali cleaning

If the mold releasing agent is calcium carbonate, unless otherwise the acid neutralization, there are no other benefits of this tank. But if the mold releasing agent is calcium stearate, earlier formed stearic acid in the acid tank will be removed from this tank. The typical temperature here also 55 Celsius and 2 w/w % KOH and 0.2 w/w % surfactant are used. The alkali level should also be higher than the coagulant level and similar to the acid level. (Bhd, 2019)

2.3.1.4 Rinsing

The objective of having rinse tanks are to remove materials on the former and neutralize the former. That is, the former is coming with high alkali content and it must be neutralized before entering to the coagulant tank. If alkali impurities go to the coagulant tank, its damages to the mold releasing agent in order to create defects in the glove. Rinse tank levels should be higher than the acid tank and alkali tank level. (Bhd, 2019; NG-K.P, 1995)

2.3.1.5 Former drying

After the rinse tank, the former has water and if this water goes to the coagulant tank, the coagulant gets diluted. this slight coagulant strength drops effect on the glove thickness. Therefore former dry oven is used to dry the former. The second objective is to maintain the coagulant tank at the required temperature. If the former is cool, then the coagulant tank heating system has to give a high heat in order to maintain its temperature and it creates small air bubbles which can result in bubbles on the former. Since air velocity inside the oven is higher, the typical temperature range of the former dry oven is 80-90 Celsius . (Bhd, 2019)

2.3.1.6 Coagulant tank dipping

Coagulant dipping is performed to a cleaned dry former. The function of the coagulant tank is to apply coagulant which is required to coagulate the latex film on the former in the latex dipping tank. Temperature maintaining inside the tank is very critical. If it is a calcium carbonate mold releasing agent, it needs a high temperature in order to keep carbonate dissolved. Here limiting factor is air bubble formation at tank walls with high temperature. The typical range is 60-65 Celsius. If calcium

stearate is the mold releasing agent, the temperature cannot be increased beyond 60 Celsius since it gets cloudy. So the typical temperature range is 55-60 Celsius for calcium stearate. The coagulant level should be higher than the latex dipping level. (Bhd, 2019; NG-K.P, 1995)

2.3.1.7 Coagulant Drying

Now on the former has coagulant, mold releasing agent, wetting agent, anti-webbing agent and water. Here water is not required. So water removing is done inside this oven. Under insufficient drying, the coagulant droplets will fall into the latex dipping tank and lump formation will happen in the latex dipping tank. The degree of drying is depending on air velocity, retention time and oven temperature. The typical range is 7 meters/second air velocity and 105 Celsius oven temperature. Here former temperature maintaining for the latex dipping also important. Typically former temperature needs to be within 50-65 range before latex dipping. Energy for coagulant drying can be saved by moisture-controlling inside the oven. Under too much coagulant drying calcium nitrate crystals will be formed at fingertips and it will create fingertip holes on the gloves. (Than.L, n.d.; Bhd, 2019)

2.3.1.8 Latex (compound) dipping

In the latex dipping tank, the film formation happens. The latex particles in the tank will be pulled toward the former by the coagulant. if the mold releasing agent is carbonate, it creates a high film thickness than the calcium stearate since large carbonate ion creates physical interactions with latex particles. Here controlling factors are TSC, pH, and temperature. TSC is the film thickness determine factor. Since formers carry out latex particles away by keeping water inside the latex dipping tank, equilibrium dipping tank TSC is lesser than the feed TSC. Typically for 8 mil dipping, it has 2% dipping TSC and feeding TSC variation. If latex tank temperature is high, the kinetic energy of the latex particles is high. So at coagulant pulling, coagulant will be able to coagulate more rubber particles. So at high dipping temperature film thickness will be high. But it cannot maintain at too high-temperature since lumps formation at high kinetic energy. If dipping temperature is too low lumps formation will also be there because of thermal shock due to high

temperature difference between latex tank and the former. Typical temperature range for the latex dipping tank is 28-32 Celsius. (Y-Tan.K, 2018; Bhd, 2019)

2.3.1.9 Gelling

To make a high thickness glove, a high gel content latex is used while low thickness has low gel content latex. The purpose of situating this oven between the latex tank and the leaching tank is to give a good wet gel strength to the film in order to protect from water. For high gel content latex, this is not required. But this is required for low gel content latex and natural latex. The gelling temperature depends on the formulation too. (NG-K.P, 1995)

2.3.1.10 Pre -Leaching

Leaching is a continuous washing process and typically a production line has 3-4 leaching tanks and freshwater consumption is around 1200 liters/10000 glove pieces. (Gazeley, 1985)

2.3.1.11 Beading

The glove beading is done by bead rollers. Beading length depends on the position of the bead roller and size (number of rounds) depend on the speed of the beading roller. The typical bead length is 10 mm and a bead has 3-4 rounds.

2.3.1.12 Curing / Vulcanization

Curing ovens are to give the required energy for cross-linking or sulphur curing. Typically curing ovens has two zones as wet zone and dry zone. In wet zone water removal is happening. Here water removing should be done gradually in order to prevent film damages due to sudden evaporation. The horizontal crack is the predominant defects at high water evaporation. Moisture controlling is very important in the wet zone in order to remove all water before entering the dry zone. In dry zone, curing is happening. Since partially curing is happening in the wet zone also, curing completion is happening in the dry zone. Here exhaust gas should be sent away due to health concerns. Here also the heat transfer depends on the temperature, air velocity, moisture-controlling system and retention time, different industries maintaining different temperature profiles. If a production line has three wet ovens and three dry ovens, as an example it can be maintained the temperature

profile in Celsius as 80, 90, 105, 110, 120,110. (Than.L, n.d.; Today-EHS, 2000; Y-Tan.K, 2018; Bhd, 2019)

2.3.1.13 Cured glove cooling

Cooling tanks are used only if online chlorination is present. After the last curing oven, the glove film has a high temperature around 90 Celsius. The effectiveness of the chlorination depends on the rate of the reaction and amount of the dissolved chlorine. As usual, high temperature increase the glove film surface oxidation reaction rate. But at high temperature chlorine escaping from the solution is high. Therefore economically viable temperature range for the chlorine tank is 30 – 40 Celsius. Former has to be cold before sending it to the chlorination tank and water is used to reduce the temperature of the glove film. Typically there are three cooling tanks and the cooling water requirement is around 1000 litres for 10000 glove pieces. Overflow of the second and third cooling tanks are re-used for the pre-leaching. But the first leaching tank over flow is drained out due to high accelerator content in that tank. After cross-linking less rubber soluble accelerators are coming to the glove surface and they dissolve in the first cooling tank water. That is the reason that the first cooling tank water draining out. Here the requirement is to maintain the last cooling tank temperature less than 45 Celsius. (Bhd, 2019)

2.3.1.14 Online chlorination

Formers are dipped in a chlorine solution. The main objective of chlorination is to reduce the tackiness of latex surface by oxidizing to help for the donning. Since natural latex is too stickier than synthetic latex, natural latex gloves need around 30 % higher chlorine concentration than the synthetic latex gloves. The typical industrial range for the chlorine concentration is 700 ppm – 1300 ppm. (V.G, 1986)

2.3.1.15 Neutralization

After the chlorine tank, residual chlorine can be there on the glove film and it may damage the glove film. Typically discoloration and plastic feeling are the tangible defects due to high/residual chlorine. So sodium hydroxide solution (a basic solution) is used to neutralize any residual chlorine. If in this tank, the sodium hydroxide concentration is high, the high water volume will be required at post leaching to

wash sodium hydroxide. So the pH of the tank is controlled and typically it will be 7-12. (Karunarathna, 2007)

2.3.1.16 Post leaching

Post leaching is done for the vulcanized film. To get help for the final glove drying, the last post leaching tank of synthetic latex gloves also kept at high temperatures. Typically there are several post leaching tanks and it has less water consumption than the pre-leaching. (Karunarathna, 2007)

2.3.1.17 Powder dipping

Typically this is an aqua solution of corn starch to reduce the tackiness of the latex surface. Here oxidation is not happened like in the chlorination. Here corn starch act as a rolling media between the glove surface and hand. Agitation is required for the corn starch solution tank in order to prevent settling. Typical concentration range is 8 – 12 % W/W. (Karunarathna, 2007)

2.3.1.18 Online Drying

Having water in the final glove can make it difficult in wearing purpose. In order to avoid accumulation of water, an online drying processing step is added to the manufacturing process. Here also the efficiency of drying depends on dryer temperature, moisture-controlling, air velocity and the retention time. Typically there are two dryers and the temperature is kept just above 100 Celsius. Insufficient drying will result in water on bead area (wet bead defect) and too much drying will result in high glove film temperature and it creates difficulties in stripping by resulting high stripping rejections. (Bhd, 2019)

2.3.1.19 Stripping

Glove stripping is done in both manually and automatically.. The advantage of manual stripping is, it has less stripping rejections due to tearing and disadvantages are high labour cost, people do not like for stripping and manual stripping is not applicable for high production line speed. Advantages of automated stripping are low labour cost and applicability of high production output. The disadvantage of automated stripping are a high initial investment and high stripping rejections. Typical stripping rejection percentage of manual stripping is 0.5% and automated

stripping is 1-1.5 %. Automated stripping is a bit difficult with natural latex gloves. (Bhd, 2019)

2.3.2 Offline chlorination process

Offline chlorination process as below (NNA-Aziz, 1993)

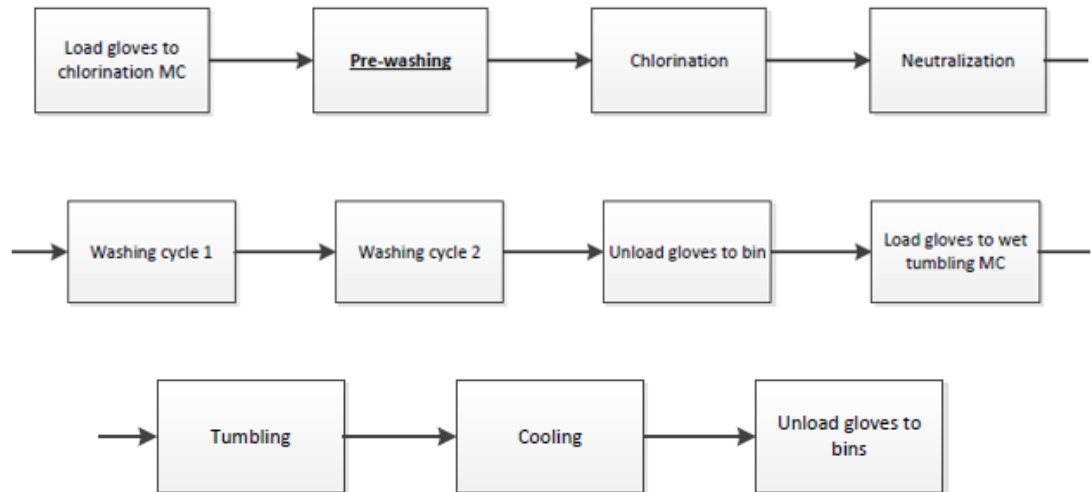


Figure 2.3-1 Offline chlorination process

2.3.2.1 Prewashing

In the chlorinator, 100 KG is the batch weight. So the first step of the chlorination process is pre-washing. Pre-washing is done with water and the main objective of pre-washing is to remove powder that is calcium carbonate mold releasing agent. This removal is economical. If there is no pre-wash cycle, calcium carbonate will react with the chlorine solution and it reduces the chlorination efficiency. So the chlorine consumption is high. Typically 300 second pre-washing is done. (NNA-Aziz, 1993)

2.3.2.2 Chlorination

After the pre-washing cycle, chlorinated water pumping starts. This pumping time depends on the pump capacities. Typically it takes 300 seconds to 500 seconds time. Chlorine concentration and the chlorination time are totally depend on the product. Low thickness gloves need a low chlorination time at low chlorine concentration

while high thickness gloves need a high chlorination time at high chlorine concentration. Typically for the high thickness nitrile gloves, 500 seconds chlorination cycle is maintained at 150 – 300 ppm chlorine concentration. Glove quality inspection is done by the AQL basis. Gloves may contain some weak points and they become holes at chlorination. Also at high chlorination, the weak areas like between fingers get holes. So some batches get hold at quality inspection after the chlorination. (Karunarathna, 2007)

2.3.2.3 Neutralization

Just after the chlorination cycle, neutralization needs to be started to neutralize the residual chlorine. Residual chlorine effect was described in the online neutralization. Typically 10% sodium thiosulfate and 5% ammonia solution is used for 300 seconds. (Karunarathna, 2007)

2.3.2.4 Post-washing cycles

The objective of this post-wash cycles is to make sure the flushing of the neutralizing solution in order to keep gloves within 6 – 9 pH range. Typically there are two post washing cycles and the cycle time of one cycle is around 300 seconds. (Karunarathna, 2007)

2.3.2.5 Tumble drying

After the post washing, the gloves are wet. So it requires to get them dried. So tumblers are used. Typical tumbling time is 3.5 hours. The drying temperature of the synthetic latex gloves is 70 Celsius and that is 55 Celsius for the natural latex gloves. Since unsaturated natural latex double bonds start degradation, natural latex cannot withstand a high drying temperature (Karunarathna, 2007).

2.4 Leaching

In disposable gloves manufacturing industry, leaching is a continuous washing process and it removes water soluble substance with water. Ideally all dipped products are leached and degree of leaching depends on the product application. The removal of water soluble things improves the film clarity and it prevents the formation of surface 'blooms' of less polymer compatible materials and reduces the

water absorption to the product. (Hashim, 2002; Gazeley, 1985; Hunda, 2014; Karunarathna, 2007)

There are two leaching methods for disposable gloves as wet and dry film leaching.

2.4.1 Wet film leaching

The leaching process which is conducted just after the gelling process is called wet film leaching. Since vulcanization has not been happened, water soluble substance migration from glove surface to leaching tank is efficient. Basically coagulant and stabilizers removal are predominant. If it is natural latex gloves production, protein removal also required.

2.4.2 Dry film leaching

Dry film leaching is carried out after the vulcanization. So efficiency of the dry film leaching is lesser than the wet film leaching. Accelerators are released after the vulcanization and they come to the glove surface since they are not soluble in polymer. So accelerator removal is predominant here. Typically final glove should be within 6 -9 ph. Range and last post leaching tank ph. Need to be maintained within that range. If it is natural latex gloves, further protein removal also focused.

2.4.3 Factors effecting the leaching

Leaching is a mass transfer process and below factors determine the efficiency of leaching

- Leaching tank temperature
- Leaching time / retention time
- Leaching flow region
- Leaching tank water quality (outside concentration)

. (Hashim, 2002; Gazeley, 1985; Hunda, 2014; Karunarathna, 2007)

2.5 Surface chlorination

If a surface of any rubber article is modified by contacting with chlorine, is called the surface chlorination. Chemical modification of rubber article is happened in order to

increase its lubricity when it contact with halogen. Out of various halogens, chlorine is widely used. But as an alternative halogen bromine also can be used.

Tackiness reduction between the glove surface and contacting surface is the primary requirement of surface modification. Since user can easily wear and remove a chlorinated glove, chlorination is widely used in glove industry. Micro texturing is the glove surface create unevenness due to chlorination. To avoid that low thickness gloves need a special care on chlorination. Below studies describe the chlorination effect further

- V.G, (1986) Crack development of the chlorinated surface of un aged and aged gloves were observed. So there was a big effect on physical structure of the chlorinated gloves. so it also change the chemical functionality of the surface. It was compared the tensile strength of 0.01% , 0.003%, 0.005%, 0.1% and 0.3% chlorinated samples after 1 minute and after 20 minutes. When it compared 0.3% sample vs 0.1% there was 9% tensile strength drop after 1 minute and 34% tensile strength drop after 20 minutes were observed
- Francis, (1987)It was found that the better industrial gloves chlorination concentration is 0.15% and chlorination time is 4.5 minutes to 7.5 minutes. (NNA-Aziz, 1993; Gazeley, 1985; Karunarathna, 2007; V.G, 1986)

2.6 Residual protein and wet look related studies

Since this was an industry-based issue, it was very difficult to find directly related publications. But it was able to find below indirectly related publications.

- A research which had been done by Hunda, (2014) for Malaysian rubber institute states that the behaviour of pre-leaching (wet film) as figure 2.6-1. By this study, it can be observed that insufficient leaching will keep substance inside the glove film.

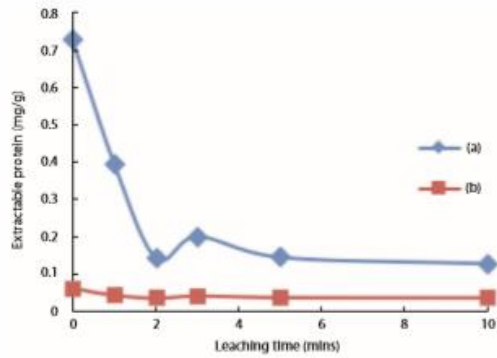


Figure 2.6-1 Leaching time vs extractable protein

Source - (Hunda, 2014)

- A research which had been done by Karunarathna, (2007) has proven that EDTA addition to the pre-wash cycle of the chlorination reduces the wet gloves as figure 2.6-2. So it proves that calcium ion cause the wet look formation.

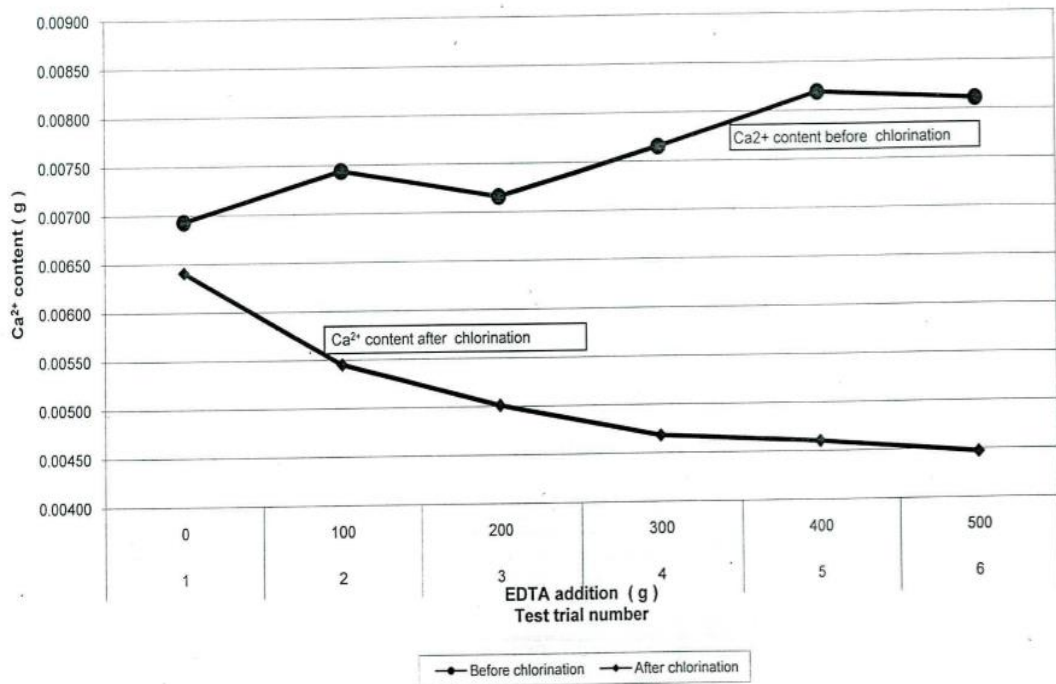


Figure 2.6-2 Calcium ion removal under EDTA

Source (Karunarathna, 2007)

- As Gazeley, (1985) explained in Leaching behaviour of pre vulcanized natural rubber latex film ,1985, the efficiency of the leaching process may have a significant effect on latex characteristics such as clarity, discoloration and blooming. In his further explanations, he had explained that water absorption into the rubber material is very high when ionic non-rubber materials like calcium two plus ions are present on the rubber surface.

**3 CHAPTER 3:
EXPERIMENTAL METHODOLOGY**

3.1 Research Plan

First it was required to identify the composition of wet look / oil mark. The first trial was designed to identify the wet look composition. To accomplish the research objectives, this research was planned to prove the below hypothesis which were made through industrial observations and literature review.

Hypothesis 01

Due to insufficient leaching, residual calcium nitrate will migrate to the surface

Hypothesis 02

Acid in the chlorination tank, will convert bead trapped calcium carbonate mold releasing agent in to calcium salt

3.2 Materials

Materials were planned under three test types as wet look composition analysing, testing for the hypothesis 01 and testing for the hypothesis 02. Compound formulation was as in table 3.2-1

Table 3.2-1 Compound formulation

Material	PHR
Acrylonitrile butadiene (41% ACN)	100.00
Ammonia Solution 23% min	0.80
Dispersion	4.23
Pigment	0.2
Vivasheild 91 76	0.28
Surfactant SABS	0.5
Potassium Hydroxide 90 % (KOH)	0.22

Dispersion formulation was as in table 3.2-2

Table 3.2-2 Dispersion formulation

Material	PHR
Titanium dioxide min 94%	0.8
Sulphur min 99.5 %	1.2
Accelerator ZDBC	0.3
Accelerator ZMBT	0.2
Zinc oxide	1.1
Ionol LC	0.5
Tamol/NN 9104	0.2
Potassium Hydroxide 90 % (KOH)	0.05

3.2.1 Wet look composition analysing

Materials

- Extracted wet look sample drop
- EBT indicator
- 0.01 M EDTA solution
- Copper sulphate

Equipment

- FTIR

3.2.2 Hypothesis 01

Here regular production condition was used. So there was no any change in the compound formulation which had been described in the specification. But dipping TSC and coagulant formulation had a slight variation than the mean specification as in table 3.2-3. Below materials were common to the both trial 01 and trial 02.

Table 3.2-3 Hypothesis 01 coagulant solution

Material	Spec.Mean W/W	Actual W/W
Calcium Nitrate	30	31
Calcium Carbonate	5	4.5
Teric 320	0.2	0.2
Freezil	0.01	NA

Critical dipping parameters are given in below points.

- Compound TSC specification mean was 40% and the actual was 39.6%
- Latex tank temperature was 29 Celsius
- Latex tank pH was 9.6

3.2.2.1 Trial 01

Materials

- 0.01M EDTA solution
- 10.5 pH buffer
- EBT indicator
- Gloves
- Distilled Water

Equipment

- Daihan Scientific Ultrasonic Cleaner Set
- Beakers
- Weighing Balance
- Pipettes
- Burettes

- Volumetric flask
- Conical flasks
- Scissor

3.2.2.2 Trial 02

Since it was a visual observation no special material requirement was there other than the common materials.

3.2.3 Hypothesis 02

Here also the regular production conditions was used and coagulant parameters as in table 3.2-4. There were three trials and materials and equipment in 3.2.3 was common to all trials

Table 3.2-4 Hypothesis 02 coagulant solution

Material	Spec. Mean W/W%	Actual W/W%
Calcium Nitrate	30	29.5
Calcium Carbonate	5	4.9
Teric 320	0.2	0.2
Freezil	0.01	NA

Critical dipping parameters are given in below points

- Compound TSC specification mean was 40% and the actual was 40.2%
- Latex Tank Temperature was 29 Celsius
- Latex Tank pH was 9.7

Materials

- Gloves
- Distilled water

Equipment

- Beakers

- Burettes
- Volumetric flask
- Conical flasks
- Scissor

3.2.3.1 Trial 01 & 02

Materials

- 37% Hydrochloric acid
- Nitrogen gas

Equipment

- Gas chromatography

3.2.3.2 Trial 03

Materials

- 99 % sulfuric acid

Equipment

- Miran setup

3.3 Method

Since some laboratory testings were common with some trials, method was divided into two as trial procedure and laboratory testing methods

3.3.1 Trial procedure

3.3.1.1 Wet look composition analysing

- Wet look sample was extracted by using a needle and FTIR spectrum was taken to wet look sample. After that spectrum was compared with the chemical library
- Cupper sulphate was added on to the wet look area

- EBT indicator was added onto the wet look area and then EDTA was added

3.3.1.2 Hypothesis 01

Under hypothesis 01, two trials were conducted as in 3.3.1.2.1 and 3.3.1.2.2

3.3.1.2.1 Trial 01

Objective of this trial was to find out the relationship between leaching time vs residual calcium nitrate

- As per the trial, a tank with trial 1 4 m length 1.5 m width was selected and filled water to 200 mm in height. The objective of selecting a large tank was to eliminate the effect to the mass transfer by changing the tank total dissolved solid content with leaching.
- Formers with gloves just after latex dipping were removed and leached in that tank by changing the leaching time
- A mild offline chlorination was given to clean the calcium carbonate after the glove stripping
- Five grams of a sample was weighted, ultra-sonic treatment was given and titrated with EDTA to measure the residual calcium nitrate weight percentage

3.3.1.2.2 Trial 02

Objective of this trial was to find out the minimum residual calcium nitrate level that wet look can observe

- The same tank as 3.3.1.2.1. was filled with water to 200mm height
- Formers with gloves just after latex dipping were removed and leached in that tank
- At different time intervals (leaching times) two samples were taken out at once
- A mild offline chlorination was given to clean the calcium carbonate after the glove stripping
- Level of the wet look was observed after 24 hours

3.3.1.3 Hypothesis 02

Under this hypothesis three trials were conducted as below

3.3.1.3.1 Trial 01

Objective of this trial was to study the glove film weaken behaviour with time at constant chlorine concentration (independent variable was chlorination time)

- Just before the online chlorine tank formers were removed with gloves
- That formers with gloves were immersed into the chlorine tank
- At different time intervals, one by one was taken out
- Time taken to permeate 37% HCL was checked for each sample

3.3.1.3.2 Trial 02

Objective of this trial was to study the glove film weaken behaviour with chlorine concentration at constant time (independent variable was chlorine concentration)

- Just before the online chlorine tank formers were removed with gloves
- That formers with gloves were immersed into baskets at different chlorine concentration
- All formers with gloves were removed at once
- Time taken to permeate 37% HCL was checked for each sample

3.3.1.3.3 Trial 03

Chemical permeation was checked at high (37% HCL) acid concentration. But in the chlorination tank, there is no such a high concentration. To interpolate data to actual production condition this trial was conducted. since the time is taken to permeate HCL was high, sulfuric acid was used for this study.

- Chemical permeation was studied with different sulfuric acid concentration

3.3.2 Laboratory test methods

3.3.2.1 Calcium nitrate identification with EDTA

This experiment had two main steps as below

Step 1 – Residual calcium nitrate extraction from the glove

- The glove sample was cut into small pieces by using the seizer
- Five grams of the sample was weighted
- 50 ml of distilled water was added
- Sonicated for 30 minutes
- The sample was filtered

Note – In ultrasonic cleaning, high-intensity and high-frequency sound waves were used to a liquid to facilitate or enhance the removal of contaminants in an ultrasonically activated liquid as water.

Step 2 - Calcium ion content analysing with EDTA titration

- 5 ml of the extracted sample was measured. colour of the sample was clear
- 3 drops of EBT indicator was added.
- 10 ml of basic buffer solution was added. Color of the sample was wine red
- Titrated with a 0.01 M EDTA solution. At the end point color changed to blue

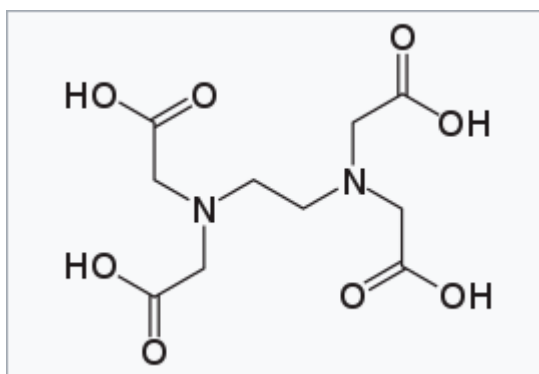


Figure 3.3-1 EDTA chemical structure

Source - (Webmd, 2017)

3.3.2.2 Chemical permeation with HCl acid

HCl is a volatile organic acid. Gas chromatography (GC) instrument was used to analyse HCl permeation. First, around 4 cm x 4 cm glove sample was cut. In GC there was a compartment made by brass and that glove piece divided that compartment into two. One side was filled with 35 ml 37% HCl acid and nitrogen gas was being circulating in the other side. Nitrogen acts as the carrier. There was a detector and it gives a millivolt signal if it can detect HCl (or organic volatile component). When HCl permeated to the other side of the compartment, nitrogen gas carried them to the detector. Usually, permeation is counted when it permeates one micrograms per square centimeter of the glove film.

Note – “Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analysing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture.”

Source - (Callemien, 2006)

3.3.2.3 Chemical permeation with sulfuric acid

Miran setup was used to analyse chemical permeation of non-volatile inorganic acids. The same as the GC, there was a compartment made with ceramic and that was divided into two by the glove sample. One side was filled with sulfuric acid and distilled water was circulated in the other side. The conductivity of the distilled water was measured. When the acid permeated to the distilled waterside, its conductivity was increased. Typically at the permeation conductivity increase to around 1000 micro cement from around 200-300 micro cement. Time taken to that conductivity increase was the permeated (breakthrough) time.

**4 CHAPTER 4:
RESULTS AND DISCUSSION**

4.1 Results

4.1.1 Wet look composition analysing

Wet look composition analysing results is given in below points

- When it was put copper sulphate on to wet look area it turned into blue colour.
- When EBT was added on to wet look area with buffer solution, it turned in to wine red and it turned again into blue under ETDA addition.
- When the wet look sample was compared with calcium nitrate under FTIR as per the figure 4.1-1, the both graphs were similar.

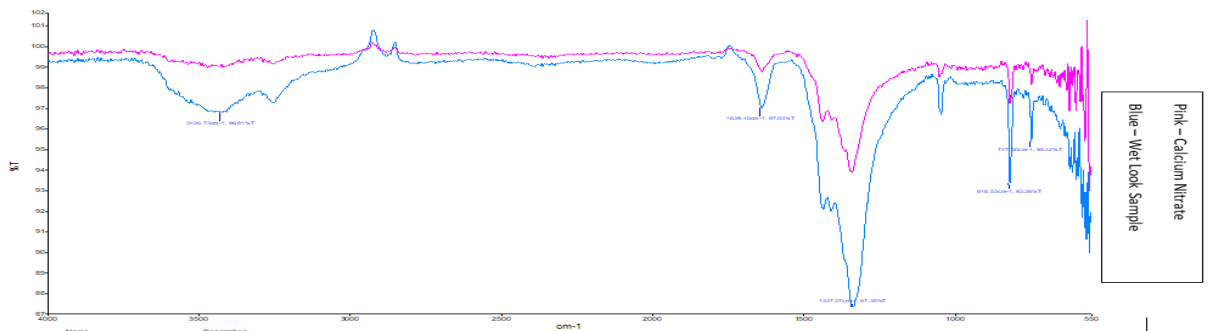


Figure 4.1-1 FTIR spectrum

4.1.2 Hypothesis 01

Results of this hypothesis is given in 4.1.2.1 and 4.1.2.2.

4.1.2.1 Trial 01

Results of the trial 01 is given in table 4.1-1 and figure 4.1-2.

Table 4.1-1 Results - Leaching time vs Residual Calcium Nitrate

Pre leached secs	Residual calcium nitrate weight %
0	2.377
15	1.420
35	1.106
75	0.385
115	0.308
155	0.250

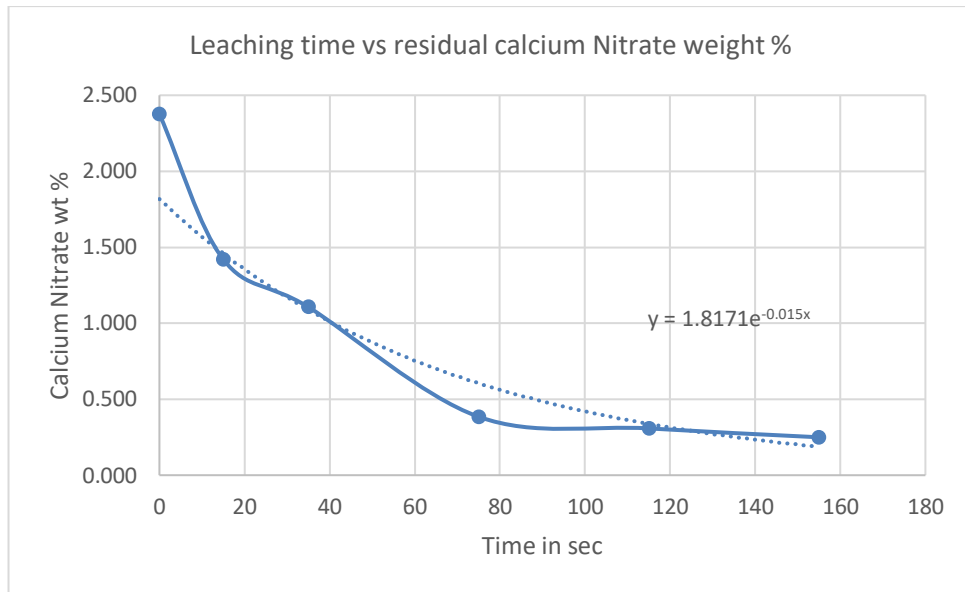


Figure 4.1-2 Leaching time vs residual calcium nitrate

4.1.2.2 Trial 02

Results of the trial two is given in table 4.1-2.

Table 4.1-2 Results - Wet look cut-off leaching

Leaching time in seconds	Wet look visual observation
0	2. oil mark
10	2. oil mark
20	2. oil mark
30	1. oil mark 1.slight oil mark
40	1. oil mark
50	No oil mark
60	No oil mark
70	No oil mark
80	No oil mark

4.1.3 Hypothesis 02

Results of the hypothesis 02 is given in 4.1.3.1 and 4.1.3.2.

4.1.3.1 Trial 01

Results of the offline chlorinated time at 1150 chlorine ppm vs time in minutes taken to permeate 37% HCL acid is given in table 4.1-3, figure 4.1-3 and figure 4.1-4.

Table 4.1-3 Results - Chlorination time vs chemical permeation

Offline Chlorinated time at 1150 ppm chlorine concentration	Time(Minutes) taken to permeate 37% HCl acid
0	452
1.5	497
3	480
5	428
8	412
12	385
20	335

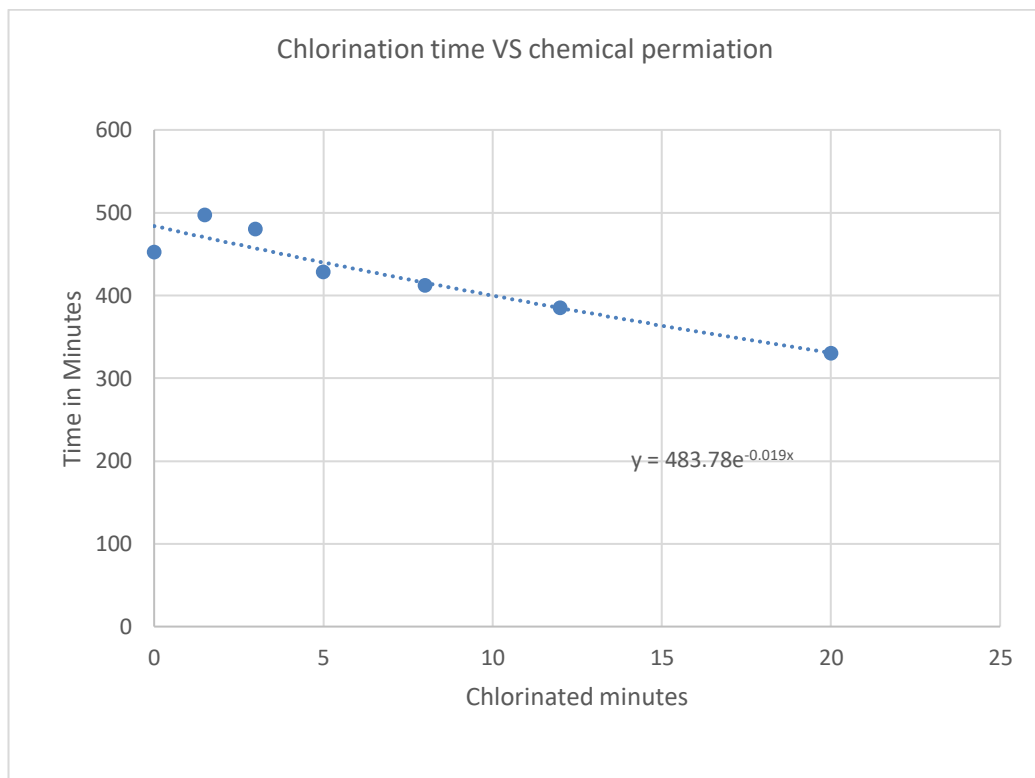


Figure 4.1-3 Chlorination time vs chemical permeation

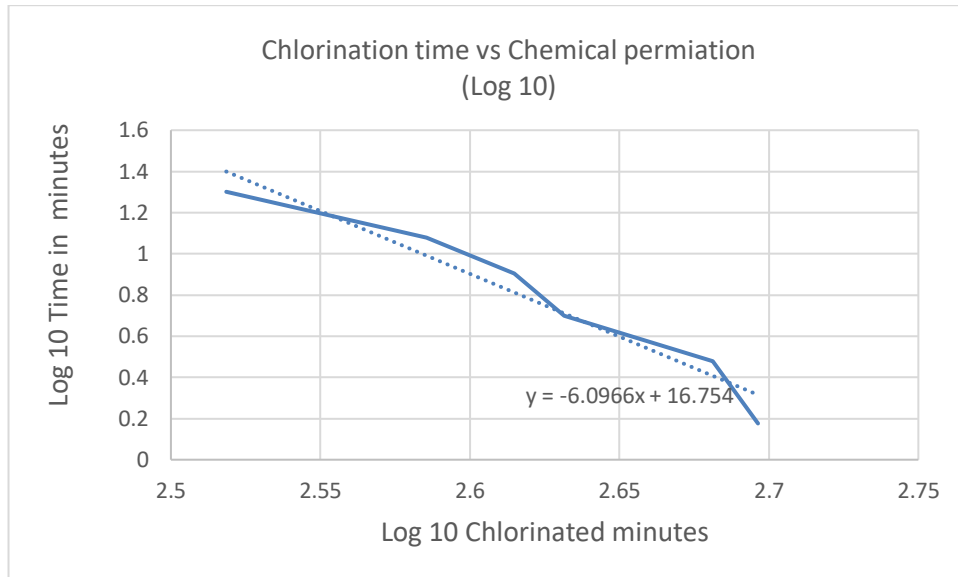


Figure 4.1-4 Chlorination time vs log chemical permeation

4.1.3.2 Trial 02

Results of Chlorine bucket chlorine concentration in ppm vs Time(Minutes) taken to permeate 37% HCl acid after 20 minutes is given in table 4.1-4, figure 4.1-5 and figure 4.1-6.

Table 4.1-4 Results - Chlorine concentration vs chemical permeation

Chlorine bucket chlorine concentration in ppm	Time(Minutes) taken to permeate 37% HCl acid after 20 minutes chlorination
1100	330
873	411
764	452
655	452
546	565
436	754

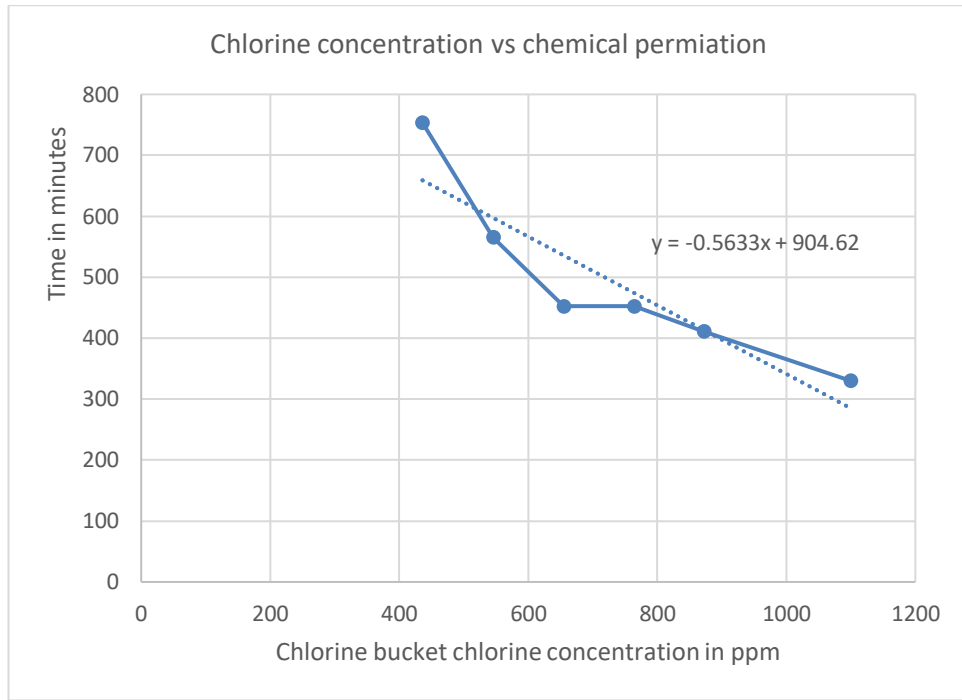


Figure 4.1-5 Chlorine concentration vs chemical permeation

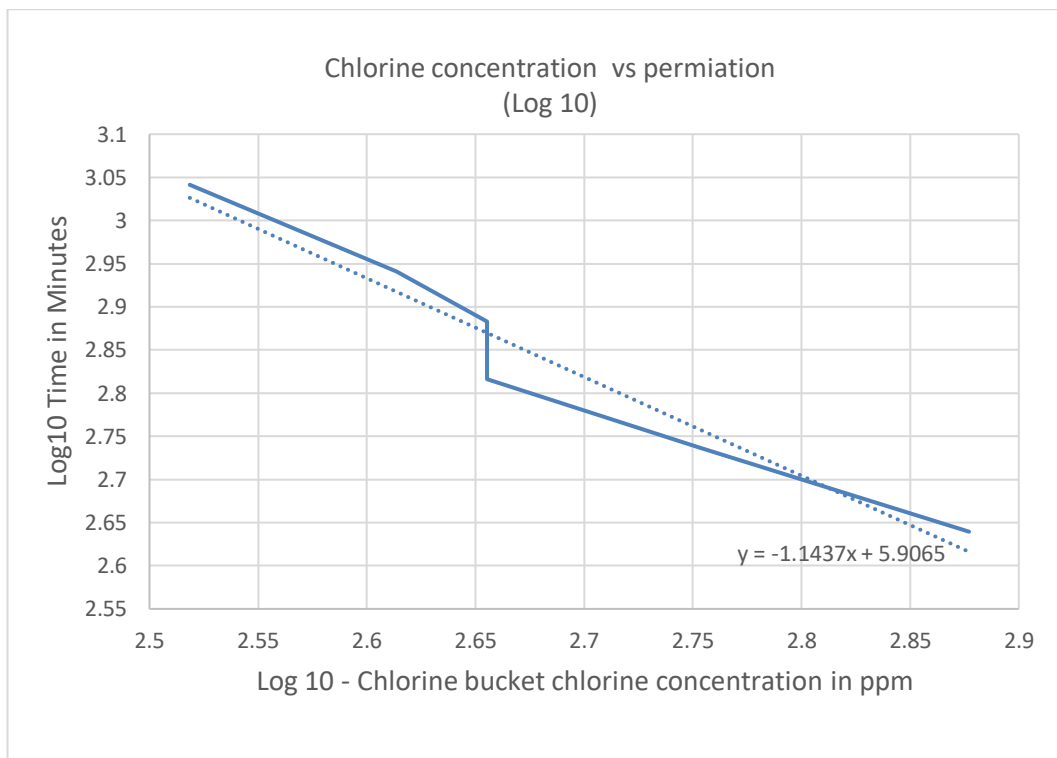


Figure 4.1-6 Log chlorine concentration vs chemical permeation

4.1.3.3 Trial 03

Results of chemical permeation against sulfuric acid concentration is given in table 4.1-5 and figure 4.1-7.

Table 4.1-5 Results - Acid concentration vs chemical permeation

Sulfuric concentration	Chemical permeated time in minutes
99	12
96	22
90	34
80	67
60	117

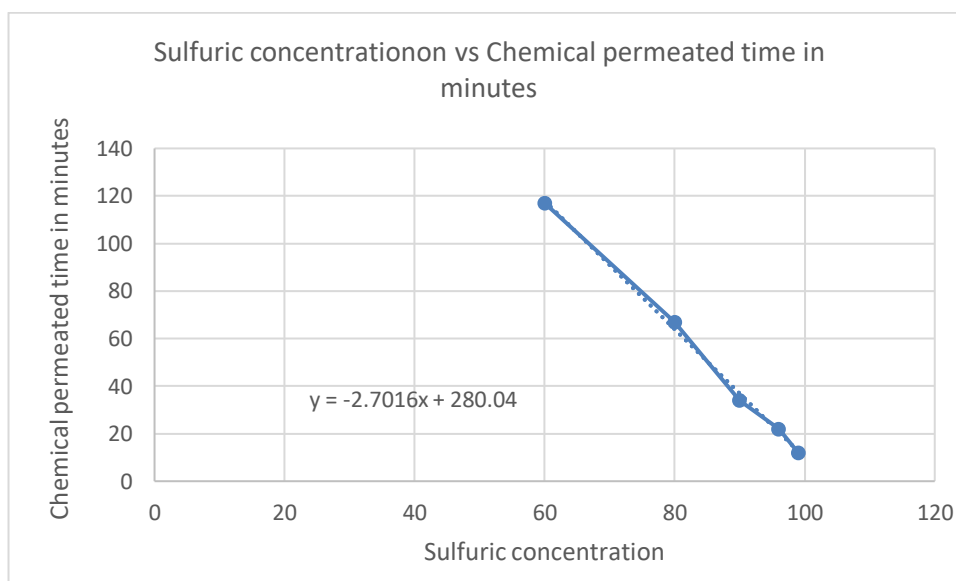


Figure 4.1-7 Acid concentration vs chemical permeation

4.2 Discussion

In the discussion, it will be mainly focusing to build up the relationships between trials and to explain them under industrial production/process conditions.

4.2.1 Wet look composition analysing

Since FTIR spectrum of the wet look sample was matched with calcium nitrate, EDTA test confirmed the calcium ion availability and copper sulphate proved that water availability, wet look consist of nothing but calcium ion and water.

There are two possible causes that Calcium ion can be available on the glove

1. Due to insufficient leaching residual calcium nitrate can be migrated to the glove surface.
2. The mold releasing agent calcium carbonate can be converted into calcium salt by hydrochloric acid which is available in the online chlorination tank / offline chlorinator.

There are two possible causes that water can be available on the glove

1. Insufficient drying in the online drying ovens.
2. Moisture which is available in the environment can accumulate on to the glove surface.

4.2.2 Hypothesis 01

By following the results of hypothesis 01 r, it can be taken the below equation

$$y = 1.8171e-0.015x$$

It can be calculated the residual calcium nitrate amount in the glove at particular time after leaching as in table 4.2-1.

Table 4.2-1 Residual calcium nitrate interpolation

Leaching time in Seconds	Residual calcium nitrate W/W %
0	1.872
5	1.736
10	1.611
15	1.495
20	1.387
25	1.286
30	1.193
35	1.107
40	1.027
45	0.953
50	0.884
55	0.820
60	0.761
65	0.706
70	0.655
75	0.608

By referring the results of hypothesis 01 trial 02, it can be observed that it needs more than 40 seconds leaching in order to wet look not appear. It takes 45 seconds as the cut off leaching time to prevent wet look defect. At the cut off leaching time, the glove will contain 0.953 W/W % calcium nitrate.

4.2.2.1 Hypothesis 01 Industrial Justification

In industry, it has around five Celsius higher leaching tank temperature than the trial room temperature condition due to former temperature carries some energy to the leaching tanks. Temperature effect in two ways for this calcium nitrate leaching as below

1. With temperature, the wet gel film tries to become in to dry condition. The dry film cannot make a way to calcium nitrate to go out. So it reduces the calcium nitrate leaching
2. Calcium ion is not soluble in acrylonitrile butadiene (synthetic latex) and it highly soluble in water. So when it increases the temperature, tendency to transfer calcium nitrate from latex to water is high. This can be further clarified under diffusion too.

As it can be understood, this is a mass transfer process. The rate of mass transfer depends on the outside concentration too. In this trial, it used a fresh and large tank. It can be assumed the zero calcium nitrate outside concentration. Since it is a continuous process in the industry, it has 3 PPT – 1 PPT calcium nitrate concentration in the leaching tanks.

The rate of mass transfer also depends on the outside flow region. In this trial, it was maintaining a static flow condition while in the industry it has a high turbulent flow condition due to the formers are moving inside the tank. So in the industry, calcium nitrate leaching may vary with the trial.

4.2.3 Hypothesis 02

Since calcium carbonate conversion to calcium salt was the hypothesis 02, there should be a clear understanding of time taken to permeate the hydrochloric acid which is inside the chlorination tank / offline chlorinator in order to convert the bead trapped calcium carbonate to calcium salt.

Here to permeate the acid through a glove film can be understood through two scenarios as below

- 1.The atomic oxygen which creates by chlorine gas reaction with water can oxidize the glove film
- 2.The acid itself has a film degradation effect and that degrade the film by making a way to go the rest of acid through the glove film. This ability depends on the acid. That is why sulfuric acid has more degradation ability than the hydrochloric acid

When the glove film contact the chlorine solution, it oxidizes the surface and reduces the surface friction by making the surface more plastic. Slight chlorination is good to improve chemical permeation properties since it makes a regular surface. That's why zero minute chlorination has low chemical permeation time than the 1.5 min chlorinated sample. But under high chlorination, the film gets oxidized and it allows acid to permeate quickly. That is why there is a chemical permeation drop with chlorination time.

Disadvantages of chlorination are it creates brittle surface, poor thermal stability, poor aging properties and discoloration after long time chlorination and the possibility of creating surface cracks. Also chlorine gas is toxic for the operators and ozone layer depletion is a main environmental issue which associates with the chlorine gas

As I explained earlier, in industrial chlorination tank or offline chlorinator doesn't have a 37% HCl concentration. So if anyone wants to use this study, there should be results in practical conditions. By referring the results of hypothesis 02 trial 03, it can be seen that there is a linear relationship between acid concentration vs chemical permeation time and that is as below,

$$y = -2.7016x + 280.04$$

since the above was for the sulfuric acid, for the HCl equation should be

$$Y = mx + C$$

4.2.3.1 Hypothesis 02 industrial justification

Since film oxidation depends on the chlorine concentration and contacting time, it was tried to make an empirical equation. To make that empirical equation, it should have more data. But in laboratory conditions, it was very difficult to maintain conditions. So this part was given up.

The above permeation test was conducted after chlorination. But in industry, permeation is happened while chlorination by acid inside the tank. So below assumption is required to justify in practical condition

Assumption – Since acid permeation starts just after gloves entering/putting to the chlorine tank/ offline chlorinator half of the chlorine concentration need to be put to the equation. The example in table 4.2-2 will elaborate it further

Example –

Table 4.2-2 Plant chlorination

Parameter	Value
Online chlorination time	2 min
Online chlorination concentration	1000 ppm (500 ppm use for the analyzing)
Offline chlorination time	25 min
Offline chlorination concentration	400 ppm (200 ppm use for the analyzing)

By referring the table in hypothesis 02 trial 01, it seems effect of 2 minutes online chlorination to the glove film is very less. That may be a positive effect too. But 25 minutes effect at 200 ppm offline chlorination is significant.

But retention time in the offline chlorinator is 25 minutes and it needs more than 200 minutes to permeate 37% HCl. Inside the offline chlorinator there is no that much of high acid concentration and that will be maximum 5 % and the time is taken to permeate 5% HCl will be too high.

Even though it can be understood that normal wet look gloves are coming due to poor leaching, there is a question why this wet look at the bead area is present?

As explained earlier Malaysian industries are the best players in the glove industry and they are getting raw materials at low prices. But in the disposable glove industry, there is a high labour involvement after stripping the gloves (after process like packing). Since labour cost is high in Malaysia, they had done much innovations on labour cost reduction. So manufacturing process controlling has not been developed. Even in Malaysian industries also most of the process controlling is depends on

operators. So below points will allow bead trap calcium carbonate conversion into calcium salt.

- Level of the leaching tank is maintained by the overflow method. If the supply water pressure drop, leaching tank levels may be low. That effects cuff leaching
- Since level of the coagulant tank keep at a higher level than the latex dipping tank, coagulant which above the film may drain to the cuff area and cuff area will have more coagulant concentration.
- There is a sodium hydroxide neutralization tank just after the chlorination tank. If its level is not above the bead level/concentration is not sufficient, chlorine will trap on the bead and it will further damage the bead in order to migrate HCL at offline chlorination
- After offline chlorination there are post-wash cycles and neutralization cycles. The functioning of them also determines the wet look gloves.
- Gloves beading is done by using beading brushes. So while beading there is a possibility of creating weak area at the bead by facilitating chemical (HCL) permeation. Failure to make the proper bead formation also there.

4.2.4 Relationship between hypothesis 01 and 02

In glove beading, the bead has 3-4 round and it claims around 10 mm total glove length. After folding, if it measures the height of the bead, it is around 2mm . So 6 mm glove length is inside the bead and calcium carbonate trapping happens inside the bead accordingly.

When it observes the glove weight reduction after chlorination is around 0.15 grams per 13.5 grams glove weight. This weight loss can be taken as the total amount of calcium carbonate inside the glove. Bead trapped calcium carbonate amount is described in table 4.2-3 and the bead trapped calcium carbonate reaction is described in table 4.2-4.

Table 4.2-3 Bead trapped calcium carbonate

Description	Figures
Glove density KG/m ³	952
Glove thickness m	0.000203
Glove Weight Kg	0.0135
Glove surface area m ²	0.069787
Glove surface area Cm ²	697.87
Calcium carbonate amount in the glove g	0.15
Glove weight of one cm ² in Grams	0.01934464
Calcium carbonate for one cm ² in Grams	0.00021494
Average bead rolling height mm	10
Bead length mm	2
Area inside the bead mm	6

Table 4.2-4 Bead trapped calcium carbonate reaction

let 1 cm horizontal length	
Description	Figures
Trapped caco ₃ in grams	0.00012896
since bead has 3-4 rounds let assume 1/3 will react at first breaking	0.00004299
bead weight in grams	0.01934464
caco ₃ trapped % which can be converted at first breaking	0.222
caco ₃ trapped % which can be converted if all reacted	0.667

If HCl which is with the chlorination reacts with the bead trapped calcium carbonate, 0.222 % calcium ion will be added to the that glove film area.

From the Hypothesis 01 discussion, it was found that 0.953 % calcium nitrate as the cut-off nitrate percentage which determines the wet look visibility. Below clarifications also are based on the that results.

If leaching time is 55 seconds, the glove film contains 0.820% calcium nitrate and that will not give any wet look. But if bead trapped calcium carbonate conversion happens, that will release 0.222% more calcium ion and the total will be 1.042 %. So wet-look can be there since it is higher than the wet look cut-off limit.

If leaching time is 65 seconds, the glove film contains 0.7060% calcium nitrate and that will not give any wet look defect. But if the bead trapped calcium carbonate conversion happens, that will release 0.222% more calcium ion and the total will be 0.928 %. Still, it is lower than the cut-off calcium nitrate percentage which is required for the wet look, the wet look will not be there.

**5 CHAPTER 5:
CONCLUSION AND RECOMMENDATIONS**

5.2 Conclusion of the study

The cuff area wet look defect comes due to the insufficient pre-leaching . The wet look defect which is seen only at the bead area comes due to the combination of insufficient pre leaching and the bead trapped calcium carbonate mold releasing agent conversion in to calcium salt. Even though this mold releasing calcium carbonate conversion happens with the acidity of chlorination, under perfect production conditions and practices, there is no relationship between chlorination time/concentration vs bead trapped calcium carbonate conversion/reaction.

5.3 Recommendations

Recommendations can be divided in to two as industrial recommendations and recommendations for future researches. In industry, it has to be focused cuff area retention time in the leaching tank in order to make sure the leaching beyond its wet look cut off leaching level. The coagulant tank level maintaining in automated ways will be better to prevent excess coagulant solution draining on to cuff area. It has to be increased the length of the glove beading unit, reduced the speed of the beading brushes and periodic lubricating the formers are very important to make sure the perfect bead formation in order to prevent bead area wet look defect.

Leaching was studied under laboratory conditions. but in the actual industrial condition, leaching temperature, turbulence and leaching tank total dissolved solid have significant impact on the leaching. By taking this study as a reference material, future researches can be planned to study the leaching in actual production condition.

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