

OPTIMUM FORMULATION FOR CURING SYSTEM

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Applied Sciences**

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In
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DECLARATION

The work described in this thesis was carried out by me at the Department of Physical Sciences & Technology, Faculty of Applied Sciences, Sabaragamuwa University of Sri Lanka, under the supervision of Dr.(Mrs).M.N.Wickramarathna ,Mrs. P.Jayabodhi and Mr.C.M.Gurugae. The report on this has not been submitted to another university for another degree.




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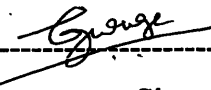


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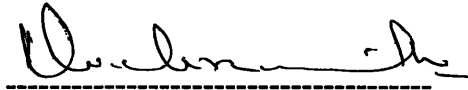
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AFFECTIONATELY DEDICATED
TO
MY EVERLOVING PARENTS AND TEACHERS

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ABBREVIATIONS

BOI	Board Of Investment
ASTM	American Society for Testing and Materials
CEN	European Community of Standards
JSA	Japanese Standards Association
pphr	Particles per dry rubber
°C	Celsius
cP	Centi Poise
Kg	Kilograms
g	Grams
MPa	Mega Pascal
%	Percentage
min(s)	Minute(s)
hr(s)	Hour(s)
EB %	Elongation Break Percentage
UTS	Ultimate Tensile Strength
min	Minimum
max	Maximum
TSC	Total Solid Content
TSI	Toluene Swell Index
OSR	Olefinically Unsaturated Rubber
NR	Natural Rubber
SBR	Synthetic rubber
RVNRL	Radiation Vulcanized Natural Rubber Latex

S	Sulpher
ZDBC	Zinc dibutyldithiocarbomate
ZDEC	Zinc diethyldithiocarbomate
TMTD	Tetramethythiuramdisulfide
ZnO	Zinc oxide
MBT	Mercapto-benzthiazole
MBTS	Mercaptobenzthiazole disulfide
TETD	Tetraethylthiuram disulfide
HEC	Hydroxyethyl-cellulose
KOH	Potassium Hydroxide

OPTIMUM FORMULATION FOR CURING SYSTEM

Dip products in the world have occupied a reputation on health protective aspects. Which is much needed in the protection of the human body to secure from harmful effects from the environment which working or living been exposed to. Dip product such as hand glove play a main role in the security and protection of human body from such harmful working and living environments.

Ansell Lanka (pvt) ltd. is one of the manufactures dip gloves for both professional and occupational purposes. In professional gloves they manufacture for both medical and laboratory usable gloves from natural and synthetic rubber latexes.

The project was to optimize the formulation for a particular glove mix. This was modified; more relevantly introduced with an accelerator called *Zincdibutylthiocarbomate* (ZDBC), which is a fast accelerator, other than the usual *Zincdiethylthiocarbomate* (ZDEC) facility itself uses. Accelerators are used to catalyze the cross linking of S (*sulpher*) bonds in between the elastic hydrocarbon polymer chains (which commonly known as *Vulcanization*). This done to improve the tensile of the glove for the donning purpose. The curing system is the oven system used for the post-vulcanization of the gloves. By accelerators pre-vulcanization facilitates.

Different ratios of ZDEC: ZDBC were introduced as 1:1, 1:0.75 and 1:0.5 into the vulcanization mixture (which includes with catalysts and sulphers) as in trials. This was subjected into the ammonium stabilized natural rubber latex mixture with some more dispersions and compounds. The curing system temperature was kept at the normal production temperature range of 100°C – 130°C.

Then the gloves manufactured were subjected to the tensile testing according to *American Society for Testing and Materials* (ASTM) standards, for further analysis of the gloves improvement. Tensile reports showed that the ratios with the 1:1 and 1:0.75 having over vulcanization within the glove, but for the 1:0.5 showed similarity with respect to the normal glove tensile specifications.

Finally it was found that introduction of ZDBC should be kept in between ratio of 1:0.75 and 1:0.5 (ZDEC: ZDBC) to have an optimum formulation, which is also possible to control the curing system for this particular glove product.

CHAPTER (01)

INTRODUCTION

1.1 Introduction

Dip product from natural and synthetic rubber (or polymer) in the world have achieved a reputation for both important in health and physical protection from harmful environment affecting to human body. Dip products such as gloves, condoms etc., are some protective barriers that could be worn for protection.

Ansell International is one of the global leaders in manufacturing health care products for different working and living environments. Their products categorize into three main sections, such as Occupational health care (Industrial gloves), Professional health care (surgical and examination gloves) and Consumer health care (condoms).

Ansell Lanka (pvt) Ltd is a daughter member of the Ansell International situated at Board Of Investment (BOI) Zone, Biyagama. They manufacture health care products for both Occupational and Professional sections. In production of both products they use natural and synthetic rubber latexes as the main raw material. Maintaining the quality of the product to the International standards is the main concern regarded for manufacturing; they manufacture the product for export purpose only, concerning the international market. Maintaining the standard tensile of the glove is one of the most important factor in the manufacture of professional gloves.

To achieve this they use vulcanizing materials and curing systems. These improve the gloves tensile strength, which is important in the donning of the glove.

The project was focused on introduction of an accelerator. Accelerators are used to catalyze the cross linking of S (*sulphur*) bonds in between the elastic hydrocarbon polymer chains (which commonly known as *Vulcanization*), into a usual glove mix to improve the tensile of a glove by changing the parameters of thermal energy usage and time of production. The project involves in optimizing the formulation for a particular

glove mix. By modifying; more relevantly introducing with an accelerator called *Zincdibutylthiocarbamate* (ZDBC), which is a fast accelerator, other than the usual *Zincdiethylthiocarbamate* (ZDEC) facility itself uses for particular glove product which the project arranged.

1.2 Overall objective

- Designing an optimum formulation of Vulcanizing Dispersion for curing system.

1.3 Specific objectives

- Study about the surgical glove latex manufacturing process in the facility.
- Study about the temperature controlling and function of the Curing oven.
- Study about rubber accelerators.
- Understand the use of **ZDEC** and **ZDBC** for the process.
- Following about Vulcanizing dispersion and mixing procedures.

CHAPTER (02)

LITERATURE SURVEY

2.1 MAIN RAW MATERIAL RUBBER AND ITS LATEX

2.1.1 About rubber tree

The **Pará rubber tree**' (*Hevea brasiliensis*), often simply called **rubber tree**, is a tree belonging to the family Euphorbiaceae and the most economically important member of the genus *Hevea*. It is of major economic importance because its sap-like extract (known as latex) can be collected and is the primary source of natural rubber.



Fig 1.1 Rubber Tree and Rubber Sap

2.1.2 Rubber Latex

Latex refers generically to a stable dispersion (emulsion) of polymer micro particles in an aqueous medium. The broadest categories of latex are natural rubber latexes and synthetic latexes. Natural rubber latexes include high ammonia latex, low ammonia latex and graft polymer latex. Latex is also used to make gloves, catheters, condoms, and is used as a binding agent in latex paint.

In the *Hevea Brasiliensis* (rubber) tree, the latex is stabilized by protein. Once it is tapped from the tree, the natural protein is susceptible to attack by bacteria upon exposure to oxygen in the atmosphere. This degradation of the protein and subsequent coagulation of the latex renders the “field latex” putrid and rancid. The field latex must therefore be preserved and fortified against bacterial attack, which is accomplished by immediately adding ammonia to the latex, since ammonia creates an environment in which the bacteria cannot survive. Field latex contains approximately 30% rubber, 5% of natural protein, fatty acids and impurities, and 65% water. In this state, it would not be economically efficient for industrial use or for

transportation. Centrifuging is the major means by which the solids concentration is increased from 30% to 60% and higher.

Creaming, another method of layer separation, is also used, but to a lesser extent. High ammonia latex is the result of increased stabilization by the addition of further ammonia following concentration of the latex. The additional ammonia raises the pH of the latex to approximately 11 to 12.

Low ammonia latex was developed because manufacturers objected to the noxious ammonia odor in their factories. A popular method to minimize the amount of ammonia in latex is to replace part of it with a combination of zinc oxide and the accelerator *Tetramethythyuramdisulfide* (TMTD). The pH of this latex is approximately 10 to 11.

2.2 SOLUTIONS, DISPERSIONS AND EMULSIONS, INGREDIENTS COMPOUNDING

2.2.1 Dispersions and Emulsions

Compounding ingredients are added to aqueous lattices as aqueous solutions if they are water soluble solids or liquids, as dispersions if they are water insoluble solids, and as emulsions if they are water insoluble liquids.

1. Particle size of dispersions and the droplet size of emulsions should as far as possible.

The primary consideration which underlies this principle is the assumption that the particles of polymer and of the compounding ingredient should be capable of mixing intimately when a solid phase separates from the compounded latex, either by cooperation or by evaporation of the dispersion medium. A secondary consideration is that sedimentation of dispersion of compounding ingredients during storage is likely to be minimizing if the particle size is reduced to that of typical latex. It is generally accepted that the particle in dispersions of solid

compounding ingredients should certainly have diameter less than 5 micrometer., and should preferably have diameter in the range 1 -2 micrometers.

2. The colloid stability of dispersions and emulsions should be comparable to that of the latex to which they are to be added.
3. pH of solutions ,dispersions and emulsions should be similar to that of the latex ,thereby minimizing disturbance of prevailing latex acid-base equilibrium by the addition of the compounding ingredients.
4. The ionic strength of the aqueous phase of the dispersion should be similar to that of the latex aqueous phase.

The particle size of dispersions of sulphur and vulcanization accelerators has no significant effect upon the progress of the vulcanization of latex deposits at temperatures in the range 100-120 °C, or upon the progress of latex pre-vulcanization at 60 °C.

Water insoluble sulphur dispersion can be incorporated to rubber latex with using water- soluble accelerator, *Sodiumdi-n-butylthiocarbamate* and a water soluble Zinc compound, Zinc acetate.

Generally, neither dry powders nor water-insoluble liquids like oils can be added to latex without disrupting the colloidal balance. Both must be processed into a form that will be miscible with the latex, as dispersion and an emulsion, respectively. The commonality is to reduce the size of the particles or droplets and to protect them so that they:

1. Will be compatible with the latex colloidal system,
2. Can be dispersed uniformly throughout the latex, and
3. Will not agglomerate or coalesce.

2.2.1.1 Dispersions

Dispersion is prepared by grinding the powder in a ball mill or attrition, with water, a dispersing agent, and a suspending agent (thickener or viscosity modifier). The use of pH modifiers and wetting agents is optional to prepare appropriate dispersion.

Ingredient	Parts
Water	47.6
pH modifier	0.1
Dispersing agent	2.0
Accelerator(powder)	50.0
Suspending Agent	0.3
Total	100.0

Table 1.1 Typical Accelerator Dispersion in 100 parts

2.2.1.2 Emulsions

An emulsion is prepared by reducing oil droplets to microscopic size in a medium that will be water-miscible. In other words, the oil becomes part of soap. It is usually made by blending a water phase and an oil phase under high shear.

Ingredient	Part
Part A	
Water	41.7
Alkali	0.3
12% Thickener	5.0
Part B	
Anti Oxidant	50.0
Fatty Acid	3.0
Total	100.0

Table 1.2 Typical Emulsion formulation in 100 parts

2.2.2 Pre-vulcanization vs. Post-vulcanization

Dip molded goods are traditionally produced from natural or synthetic rubber latex by, Immersing shaped formers into a tank filled with compounded latex, Withdrawing the formers from the bath, Drying the water out of the film in a hot air oven, and Vulcanizing the resultant film at an elevated temperature.

The individual rubber particles in the latex may have already been at least partially vulcanized prior to the shaped formers being dipped into the latex. If the latex is not pre-vulcanized prior to the dip molding of the formers, then the latex process is considered to be a post-vulcanization process. Often, pre-vulcanized latex is used for dipping, and the dried rubber films are then further vulcanized in a post-vulcanization process to obtain improved tensile properties. The use of pre-vulcanized latex has advantages, in that the wet and dry gel strength of the dipped film is generally improved, compared to latex that is not pre-vulcanized. The total process time is reduced, since only a limited amount of time (if any) is devoted to vulcanizing after dipping and drying. Details of these methods are well known.

2.2.3 Superior Particle Integration

It is believed that particle integration may be improved upon if at least some post-vulcanization is allowed to take place. The post-vulcanization step is presumed to provide for covalent bonds between individual coalesced rubber particles, not just within the individual particles as is the case in pre-vulcanized films. In both of these processes, the latex particles are not necessarily uniformly vulcanized, since the outer surfaces of the particles are more directly exposed to the vulcanizing agents, in contrast to the interior of the particles. If the outer surfaces of the particles are more cross-linked than the interior of the particles, then a pseudo case hardening effect may have occurred. Some manufacturers allow latex to Amature in

an effort to allow the cross-links to become more evenly distributed throughout the film (Dzikowicz, 2003).

2.2.4 Pre-vulcanization Methods

As a general rule, sulfur is used as the primary vulcanizing agent for dip molded latex rubber components. Various accelerators, activators, sulfur donors, and boosters are necessary to properly compound these lattices for use in traditional dip molding vulcanization processes. The pre-vulcanization of latex rubber without the use of these types of chemicals, or with no chemicals at all, by means of free radical cross-linking is well known. These methods rely on high-energy irradiation. NR latex exposed to high-energy irradiation is referred to as Radiation Vulcanized Natural Rubber Latex (RVNRL). Often, a chemical sensitizer is used in combination with irradiation to achieve the desired properties. The tensile strength for rubber films made from this type of latex can be very good. No additional post-vulcanization is done after the film is formed, so this process would be considered a pre-vulcanization process. While the tensile strength of dipped films made with this type of latex is adequate to meet the requirements of many dip molded rubber devices, such as surgical gloves, the tensile strength of these films is not as high as found in many traditionally pre-vulcanized latex films, which incorporate a post-vulcanization step. The 100% tensile modulus values are also much lower than for conventional vulcanized NR latex films. There appears to be no known chemical method available to allow for true covalent bonding between integrated particles within these dipped films (Dzikowicz, 2003).

2.2.4.1 Cross-linkers

Vulcanization creates a “memory” in a rubber polymer. After the stress or strain of distortion or stretching is removed, the polymer returns to its original shape. This is what distinguishes a rubber from a thermoplastic. It is accomplished by connecting the molecular chains of the polymer to each other.

Cross-linkers are the chemicals that connect these molecular chains. Since the chains are linked, a force is required to pull them apart. The strength of this force is a measure of the efficiency and number of connectors or cross-links. The force required to stretch a cross-linked polymer to a specified elongation is called a modulus. The force required to completely separate a cross-linked polymer is called the tensile strength.

There are some types of cross-linking agents for vulcanization process. Elementary sulfur, Thiuram polysulphides and Xanthogen polysulphides are some cross-linking agents (Dzikowicz, 2003).

(A) Sulphur

It is the universal cross-linking agent for natural rubber. 1-2 pphr (particles per rubber) should be introduced to latex with good quality. In the past water soluble polysulphides are also been used.

By the cross linking mainly 3 types of sulphur cross linking takes place. They are, Mono-sulphidic, Di-sulphidic and Poly-sulphidic cross-linkings. Where as Poly-sulphidic cross-linking imparts high tensile strength at any given cross-links concentration, Mono-sulphidic cross-links are more stable thermally. In the case of sulphur vulcanized derived from in the latex form, the formulations are the conditions of vulcanization employed are usually such that predominantly poly-sulphidic cross-links are expected to form initially. however, it is possible that some rearrangements to other type may occur during post-treatment of vulcanizate. two factors favor the initial formation of poly-sulphidic cross-links, rather than of mono-sulphidic and di-sulphidic, in vulcanizate from the lattices to sulphur is usually in the range regarded by rubber technologists as being convectional, rather than being such as to comprise a so-called efficient vulcanization system; for the latter, the ratios of accelerator to sulphur are higher. The other factor favoring the

formation of poly-sulphidic cross-links is that temperatures of vulcanization are relatively low (Dzikowicz, 2003).

(B) Thiuram polysulphides (TPS)

Vulcanizing agent for several Olefinically Unsaturated Rubber (OSR) is elementally sulphur. Vulcanizates obtained in this way are superior to conventional sulphur vulcanizates, where optimum heat-resistance is required, or where it is desirable to keep the sulphur concentration as low as possible. An important additional characteristic of OSR vulcanized by TPS in the absence of elemental sulphur is their excellent resistance to oxidative degradation catalyzed by transitional-metal compounds such as Cu(copper).

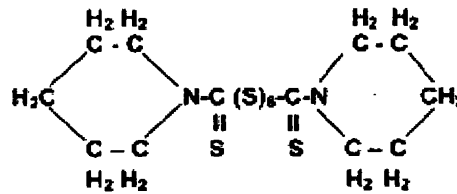


Fig 1.2 Dipentamethylenethiuram hexasulfide

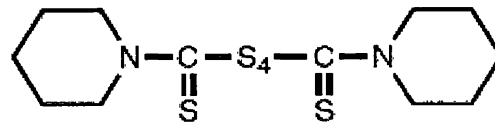


Fig 1.3 Dipentamethylenethiuram tetrasulfide

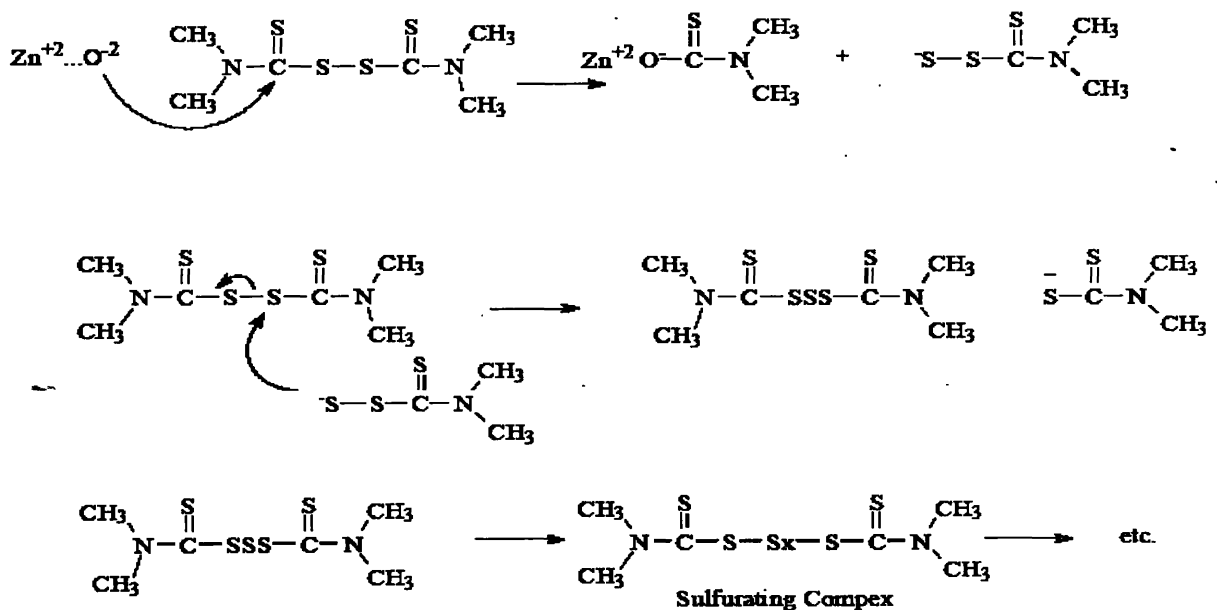


Fig 1.4 Tetramethyldisulphide thiurams as Sulfur Donors

2.2.4.2 Activators

Sulfur alone will vulcanize (cure or crosslink) rubber latexes. However, at elevated temperatures, the process will theoretically take days, during which time oxidation would destroy the polymer before sufficient cross-linking could take place. Zinc oxide activates the cross-linking action of the sulfur. A sulfur/zinc oxide cure of rubber latex can take place in a matter of hours at elevated temperatures, subject to the degrading effects of oxidation.

The effect of such activators is to increase the properties of tensile strength and modulus. Effect of increasing the level of Zinc oxide (**Fig 1.5**) upon the development of the tensile strength of natural rubber latex films post-vulcanized with 1 pphr of sulphur and 1 pphr of *Zinc di-n-butylthiocarbamate* (ZDBC) as accelerator. The rate of vulcanization was little affected by the level of Zinc oxide, in the optimum tensile strength was always attained after approximately the same period of vulcanization (20 – 25 min at 93°C).

Zinc oxide behaving as a reinforcing filler in the rubber film, partly because the level were too low for the reinforcing effect to be apparent, and partly because particulate filler do not significantly enhance the tensile strength of films from rubber lattices, even if they do enhance the tensile strength of film from bulk rubber. Resistance to over-vulcanization is also improved by the presence of a zinc compound such as Zinc oxide (The level of Zinc oxide should be at least 0.5 pphr).



Fig 1.5 Physical appearance of ZnO

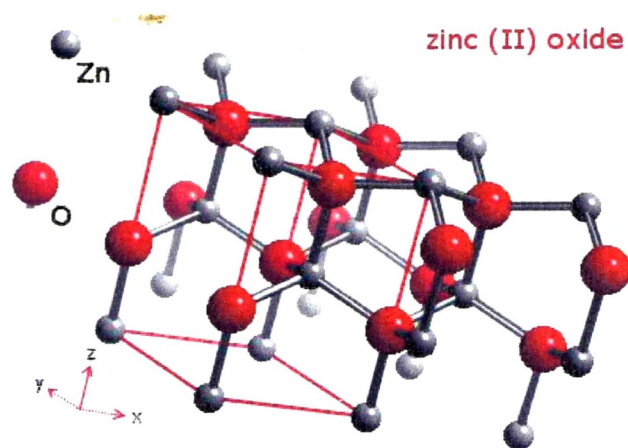


Fig 1.6 Structure of ZnO

2.2.4.3 Accelerators

Accelerators have made latex a viable industry, and have made latex products readily available worldwide by reducing their cure time to minutes. Most accelerators for sulfur cures are nitrogen-bearing. They fall into classes called dithiocarbamates, thiurams, sulfenamides, and thiazoles. The xanthates are an exception because they do not contain nitrogen. Guanidines and thioureas accelerate the zinc chloride cross-linking of poly-chloroprene. Accelerators for metal oxide cross-linking in a carboxylic polymer are not necessary unless a dual system of metal oxide and sulfur vulcanization is required for optimum properties (Dzikowicz, 2003).

The combination of cross-linkers, activators and accelerators not only determines the rate of cure, as mentioned, but the state of cure. It is the responsibility of the latex chemist to optimize the desired physical properties of the finished article by manipulating the levels of the cross-linker, the activator, and the accelerator. In the case of natural rubber latex, vulcanization can take place in the colloidal state; rapid cures may therefore not always be desirable (Dzikowicz, 2003).

(A) Primary accelerators

Primary accelerators the major group used in tire manufacture is formed by sulfenamides. These are produced by an oxidative coupling reaction of *Mercapto-benzthiazole* (MBT otherwise called *Mercaptobenzothiazole*) with a primary amine like cyclohexylamine or tert-Butylamine. Secondary

amines like di-cyclohexyl-amine can be used also but result in much slower accelerators. Such a slow accelerator is required in the steel cord adhesion compound mentioned above, because for optimal adhesion a slow cure is required. Another important group of primary accelerators is formed by the thiazoles. The two main products are *Mercaptobenzthiazole* (MBT) and *Mercaptobenzthiazole disulfide* (MBTS), a product formed by oxidative coupling of two MBT molecules. The thiazoles are used for the vulcanization of thick articles, and as basic accelerator in *Ethylene-propylene-diene* rubbers (EPDM) compounds, in combination with mixtures of ultra-accelerators (Dzikowicz, 2003).

(B) Secondary accelerators

Secondary or ultra-accelerators the main categories are the thiurams and the dithiocarbamates. In vulcanization of tire compounds they are used as small addition to sulfenamides to boost the speed and state of cure. They have a very vulcanization speed and therefore, next to boosters in tire compounds they are used as main accelerator in EPDM compounds and in latex compounds. EPDM compounds have much less cure sites than natural rubber or SBR, and therefore need a rapid vulcanization system to have sufficient cure speed. Latex is cured at relatively low temperature (100- 120 °C) and therefore need an inherently rapid accelerator. The major thiurams used are *Tetramethylthiuram disulfide* (TMTD) and *Tetraethylthiuram disulfide* (TETD); they are produced by the reaction between *dimethylamine* or *diethyl-amine* and *carbon disulfide*. The major dithiocarbamates are the zinc salts *Zinc diethyldithiocarbamate* (ZDEC) (Fig 1.7) and *Zinc dibutyldithiocarbamate* (ZDBC also known as *zinc di-n-butyldithiocarbamate*) (Fig 1.8) (Dzikowicz, 2003).

By comparing the activity of ZDEC and ZDBC, ZDEC is least active than ZDBC. The principle reason for this effect of alkyl chain length upon activity as an accelerator of sulphur-vulcanization is probably that the solubility of the *Zinc dialkyldithiocarbamate* rubber tends to increase as size of the alkyl group increases. However, caution must be exercised in inferring from behavior in films from lattices of other Olefinically

Unsaturated Rubbers (OSRs). The behavior of vulcanization accelerators in films from natural rubber latex is affected by the presence of various non-rubber substances which function as accelerator activators, as well as by the ammonia which is usually present as preservative (Dzikowicz, 2003).

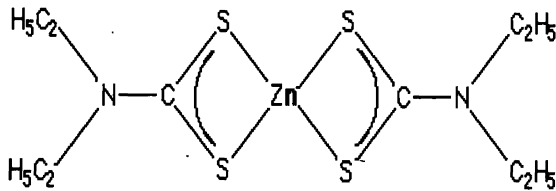


Fig 1.7 Zinc diethyldithiocarbamate

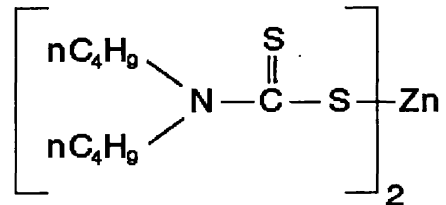


Fig 1.8 Zinc dibutyldithiocarbamate

(I) Zincdibutyldithiocarbamate (ZDBC)

Major Application and properties of ZDBC:

ZDBC is used as secondary ultra accelerator for thiazole and sulfonamide cure systems in

general purpose polymers (NR, SBR and EPDM). It can be used as a primary accelerator in specialty applications as well as in latex.

In latex applications ZDBC is mainly used in transparent goods and in pre-vulcanized latex. An additional application is as an antioxidant in adhesive systems. ZDBC gives faster cures than ZDEC.

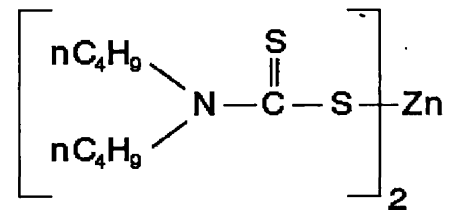


Fig 1.9 ZDBC

Some compounding information:

In NR latex, when used as a primary accelerator 1 pphr of ZDBC with 2.5 pphr sulfur is a good starting point.

In ZDBC has the highest solubility of all *dithiocarbamates*, offering the lowest blooming effect.

In rubber cured in contact with polyester textiles ZDBC is preferably used over other *dithiocarbamates*.

(II) Zincediethyldithiocarbamate

Major Application and properties of ZDEC:

ZDEC is a secondary ultra accelerator for general purpose polymers (NR, SBR, IIR and EPDM). It can be used as primary accelerator in some continuous cure applications as well as in latex.

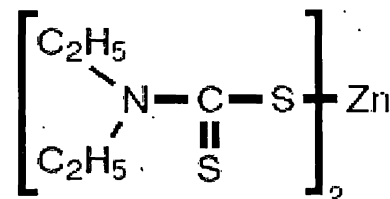


Fig 1.10 ZDEC

Furthermore ZDEC is used as an antioxidant in adhesive systems.

For latex applications three special grades are available: a dispersible powder, a wettable powder and a wettable granule.

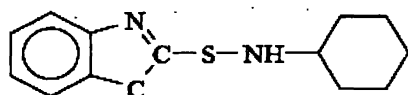
It should be noted that in the application of ZDEC N-nitrosodiethylamine can be formed by the reaction of diethylamine, a decomposition product, with nitrosating agents (nitrogen oxides).

Some compounding information:

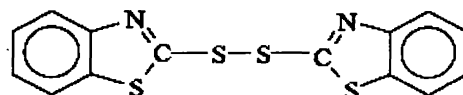
In Natural Rubber (NR) latex 1.0 pphr ZDEC together with 2.5 pphr sulfur serves as a good starting point when used as a primary accelerator.

A good starting point for foamed applications based on NR or Synthetic rubber (SBR) is 1.5 pphr ZDEC in combination with 1.0 pphr 2.5 pphr sulfur.

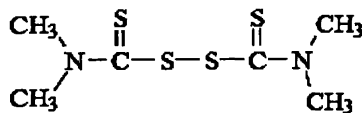
In NR ZDEC is generally used at the 0.1 to 0.4 pphr level in combination with thiazoles and sulfenamides.



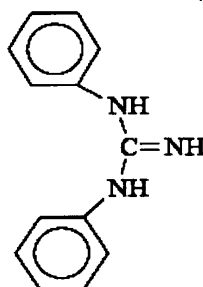
Cyclohexyl benzothiazole sulfenamide



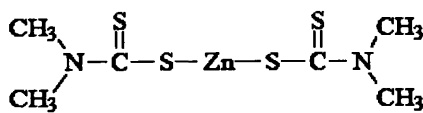
Mercaptobenzothiazole disulfide



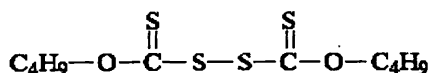
Tetramethylthiuram disulfide



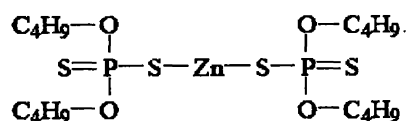
Diphenyl guanidine



Zinc dimethyldithiocarbamate



Dibutyl xanthogen disulphide



Zinc Dibutylphosphorodithiate

Fig 1.11 Structures of Selected Accelerators

(III) Thiuram Accelerated Vulcanization

Although *thiuram* and *dithiocarbamate* accelerators form nitrosamines, a number of published formulas use these components as vulcanization agents. For completeness, we include the mechanism by which this class of materials is thought to function¹⁴; however, again we recommend the use of alternative *nonnitrosamine*-generating accelerators. Thiuram accelerated systems participate in the vulcanization process through formation of a zinc complex as shown in Figure 11. The sulfur rich complexes are formed by insertion of the sulfur into the *zinc dimethyldithiocarbamate* molecule, which in turn is an active sulfurating complex. Rubber bounded intermediates are subsequently produced followed by cross-linking to form polysulfidic cross-links. These polysulfidic cross-links evolve into mono--sulfide and disulfidic cross-links (Dzikowicz, 2003).

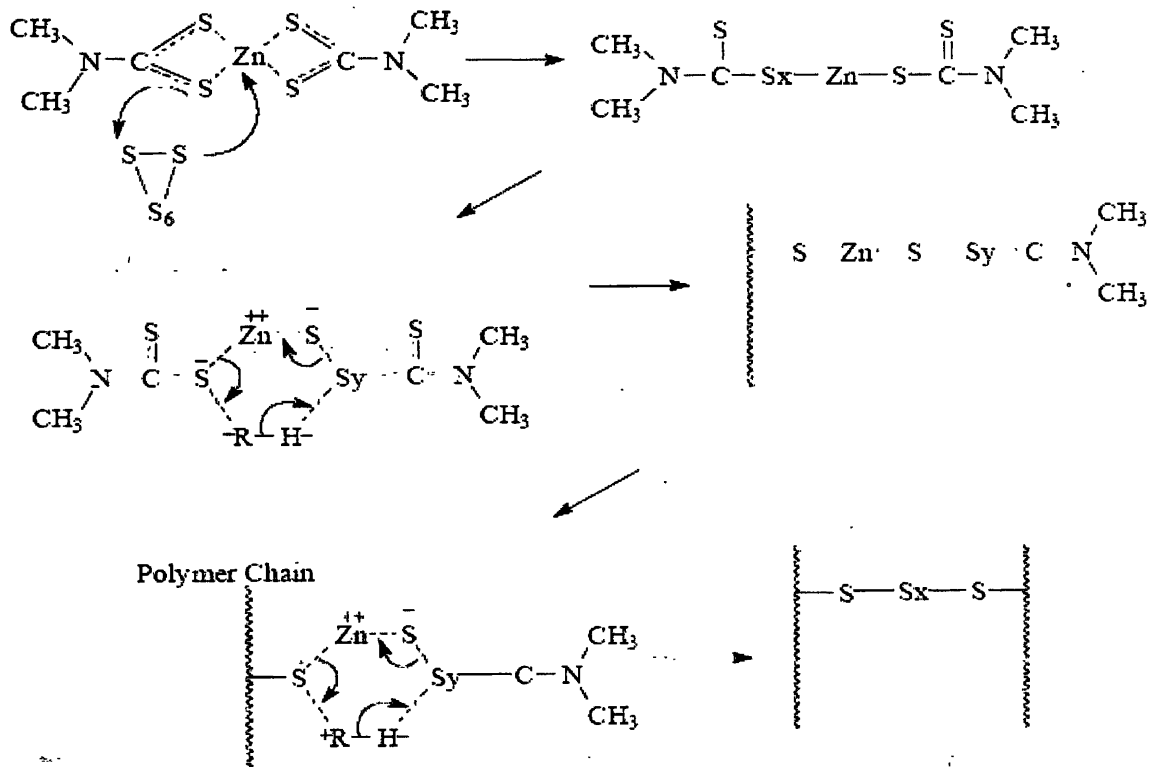


Fig 1.12 Possible Mechanism of Thiuram Accelerated Vulcanization

2.2.4.4 Antioxidants

Oxygen attacks and degrades latex rubber films in the same manner that it degrades dry rubber products. The process by which antioxidants deter oxidation. Two major types of antioxidants used for latex, the phenolic types are found in most applications. While their performance is not as efficient as the amine types, their minimal staining and discoloration are preferred for gloves, condoms, balloons, thread, foam and carpet backing. Amine antioxidants are limited to products where staining and discoloration are of no consequence, such as some adhesives and saturants for paper, and non-woven coatings that will be manufactured into gasketing products (Dzikowicz, 2003).

Antioxidant Synergists

The major difference in oxidation between latex films and dry rubber products occurs during the vulcanization cycle. Most dry rubber products are cured in closed molds which excludes air and, therefore, oxygen. Vulcanization and the subsequent development of physical properties are allowed to proceed uninhibited, without the interference of oxidation.

Most latex products are cured in circulating hot air ovens. From the very moment that the latex film dries and the water evaporates, it is open to attack by oxygen. During the cure cycle, vulcanization (cross-linking) can be inhibited by oxidation. At the same time that physical properties are being generated, oxygen attack is destroying them. Therefore, a good antioxidant synergist is required to minimize oxidation and permit cross-linking to build physical properties quickly and efficiently. *2-mercaptotoluimidazole*, and its zinc salt, are effective antioxidant synergists for that purpose. They should always be used with an antioxidant (Dzikowicz, 2003).

2.2.4.5 Film Surface Conditioners

A common latex film defect, especially with synthetic latexes, occurs upon drying. The evaporation of water causes the film to shrink, which creates striations, valleys and “mud cracks” in the surface of the film. The exact cause of this phenomenon is unknown. A surface conditioner like sulfated methyl-oleate can relieve the internal stress of the drying film to reduce shrinkage, thereby eliminating or decreasing these defects (Dzikowicz, 2003).

2.2.4.6 Thickeners

The viscosity of natural rubber latex is not easily modified, and the addition of compounding ingredients and decreases in pH makes it difficult to keep the viscosity under control. Except for SBR, synthetic latexes almost always require a thickening agent to facilitate dipping and coating operations. Viscosity plays a key role in building film thickness and suspending dispersed compound ingredients.

There are two general types of thickeners: polymeric and mineral. Water soluble polymeric, whether synthetics like polyacrylates and polyvinyl alcohols or natural gums like cellulosics and alginates, thicken latex by virtue of their very long molecular chains. Mineral thickeners like bentonite and smectite are very hygroscopic and swell in the presence of water to many times their original particle size (Dzikowicz, 2003).

Hydroxyethyl-cellulose (HEC) is a medium-high molecular weight cellulosic polymer used as a general thickener for water-borne systems including latex paints, personal care products, and household cleaning products.

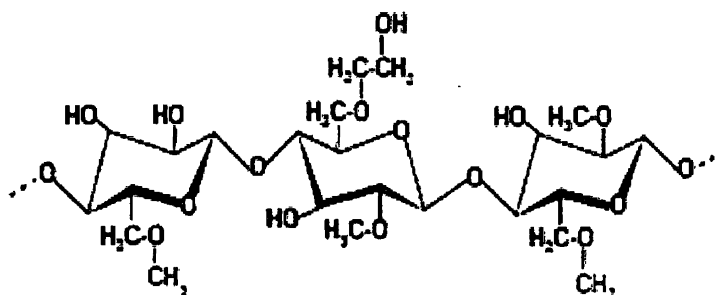


Fig 1.13 HEC polymeric part

Typical Properties[†]

Characteristic	Range
1% Brookfield viscosity	1500 to 2400 cP
Water insolubles	1.00%, maximum
Volatiles	5.0%, maximum
Solution pH (2%)	6.0 to 7.0
Hydration time (pH 7.2 buffer)	5 to 15 minutes
Particle size through #20 mesh	98%, minimum

Table 1.3 Typical Properties of HEC

2.3 MACHINE PROCESS

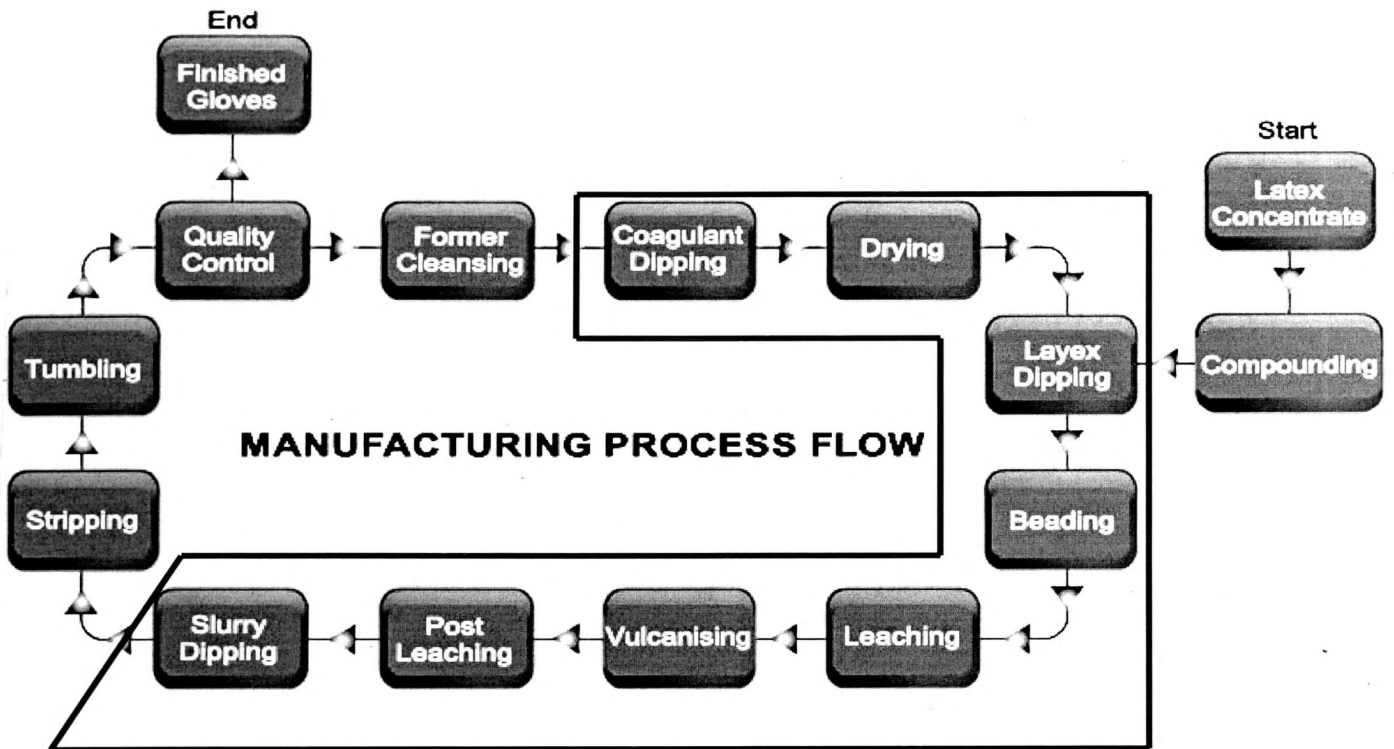


Fig 1.14 Overall Machine Process

2.3.1 Dipping

The largest application by far for latex is the dipped goods industry. This is the process by which:

1. A latex compound is made to coagulate on a former or dipping mold,
2. The latex compound is dried and vulcanized on the former, and
3. The finished product is stripped from the former.

Unsupported gloves and balloons are made by the coagulant dip process. The former, usually ceramic, is dipped into a first bath filled with an electrolytic solution. This solution (usually calcium nitrate or calcium chloride), upon drying, leaves a uniform coating on the former. The coating is totally incompatible with the latex. Therefore, when the former is dipped into a second bath of the latex compound the coating destroys the latex stability in its immediate area. When the former is removed from the

bath it is coated with a gelled film of latex compound. A third bath filled with warm water acts as a leaching tank. In it all water-soluble materials like coagulants, stabilizers, dispersing and wetting agents, pH modifiers and water-soluble thickeners are removed and carried away from the gelled film on the former. Then the former proceeds to a circulating hot air oven where the film is dried and vulcanized. There is some residual tack to the latex product. Dusting and/or chlorination operations are designed to remove the residual tack of the polymer and allow for the easy donning of gloves. They can be performed on line (before the product is stripped from the former) or as a post-treatment. Their use also permits the packaging of many gloves in the same box without them sticking to each other.

A similar process is involved in heat-sensitized dipping. The difference is that a heat-sensitizing chemical is compounded into the latex. The former, usually aluminum instead of ceramic, is heated or warmed. When the warm former is immersed in the latex compound, the heat sensitizer is activated to coagulate the latex on the former. This eliminates the need for an external coagulant and the coagulant dip bath. Thin-walled latex products like condoms and membranes are dipped and processed without the use of any coagulants. This is called straight dipping. Supported gloves like chemical handling and industrial gloves are manufactured without the use of coagulants, but the former is covered with a fabric called a liner (the support for the coating). The assembly is dipped in the latex compound and dried and cured in an oven. The gloves are rarely leached to remove water soluble materials.

Controlling these processes with regard to compound stability, viscosity, coating weight pick-up, line speed, and drying and curing times are essential skills for manufacturers, and matters beyond the present discussion. Nevertheless, the reader can appreciate the importance of technique in dipping operations.

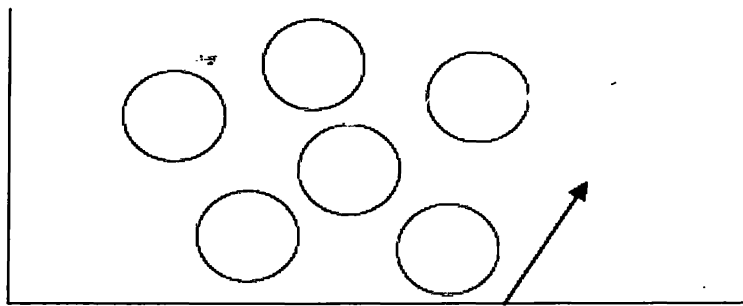
Pre-vulcanization, Maturation and pre-curing

Natural rubber latex can be cross-linked in the colloidal state. This process is called pre-vulcanization. When the water is removed from the pre-vulcanized film or finished article, a degree of cross-linking has already occurred. The film should not be fully vulcanized; however, the cross-linking that has occurred enables the manufacturer to decrease the time required for an optimum cure in the circulating hot air oven. An additional benefit is that less time at elevated temperatures means less opportunity for oxidation degradation.

Pre-vulcanization is accomplished by introducing the dispersed ingredients of the cure system into the latex and elevating the temperature for a period of time. Through the use of ultra accelerators like the dithiocarbamates, the temperatures and the holding periods have been reduced. This advance in latex technology does not come without the introduction of a new consideration, an increase in the maturation rate.

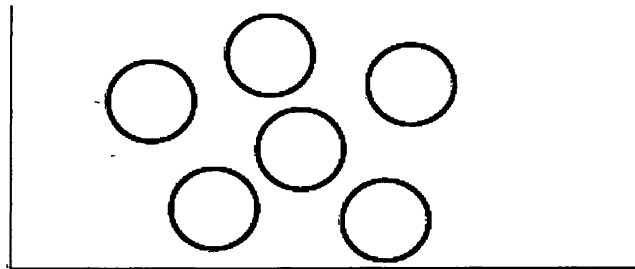
Maturation is the slower but continuous cross-linking that takes place at room temperature with ultra accelerators. When cross-linking proceeds too rapidly during maturation, the compound will be difficult to process, the viscosity will increase, and the resultant dried films will have poor physical properties. This advanced and undesirable state of cross-linking in colloidal suspension is termed pre-cure.

While the use of pre-vulcanization is very desirable for more efficient latex processing, a careful balance must be struck in the maturation process in order to secure the advantages of pre-vulcanization without the high risk of continuing into pre-cure, with its negative effect on final film properties.



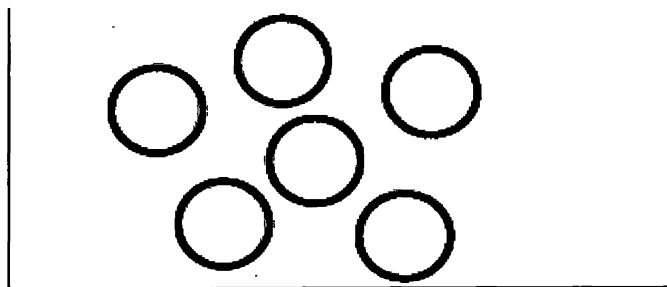
Particles dispersed in aqueous phase are separate, uncrosslinked, and homogeneous throughout.

Fig 1.15 Latex Particles in Colloidal Suspension



Dispersed particles, still separate but lightly crosslinked.

Fig 1.16 Particles with Pre-vulcanization



Particles with crosslinked surface and very slightly crosslinked interior.

Fig 1.17 Particles with pre-cure



Upon drying, precured particles agglomerate and form only a weak film because the thick particle skin interferes with homogeneous vulcanization.



Prevulcanized particles agglomerate and form a good film with homogeneous crosslinking.

Fig 1.18 Agglomeration upon drying and pre-vulcanizing

2.3.2 Pre-leach and Post-Leach(dry-film leaching) process

This series of leaching is to remove any residual coagulant from the glove.

After dipping in latex tank the glove were subjected into a hot water tank for pre-leaching, to remove chemicals from the gelled glove and other residues, before drying and curing ovens. Wet-gel leaching and beading: The thin latex film on each former is partially dried and leached briefly in clean water to remove the water-soluble materials. After the curing of the gloves the gloves are again subjected into a water tank for post-leaching. Post-cure leaching or dry-film leaching: The cured gloves are immersed in clean water tanks to remove more water-soluble substances, particularly proteins on the surface of the gloves.

2.3.3 Drying and curing

The gloves are then dried and vulcanized. Drying and vulcanization or curing of the gloves are usually done in hot-air ovens, initially at lower temperatures of 80°-90° C, and then at higher temperatures of 100°-140° C where necessary.

2.3.4 Overall Surgical Gloves Process

The surgical gloves producing process had same sequence. But there were small changes. These all machines were cam operated. That is the dipping action was achieved by making angles on the tracks through the production line.

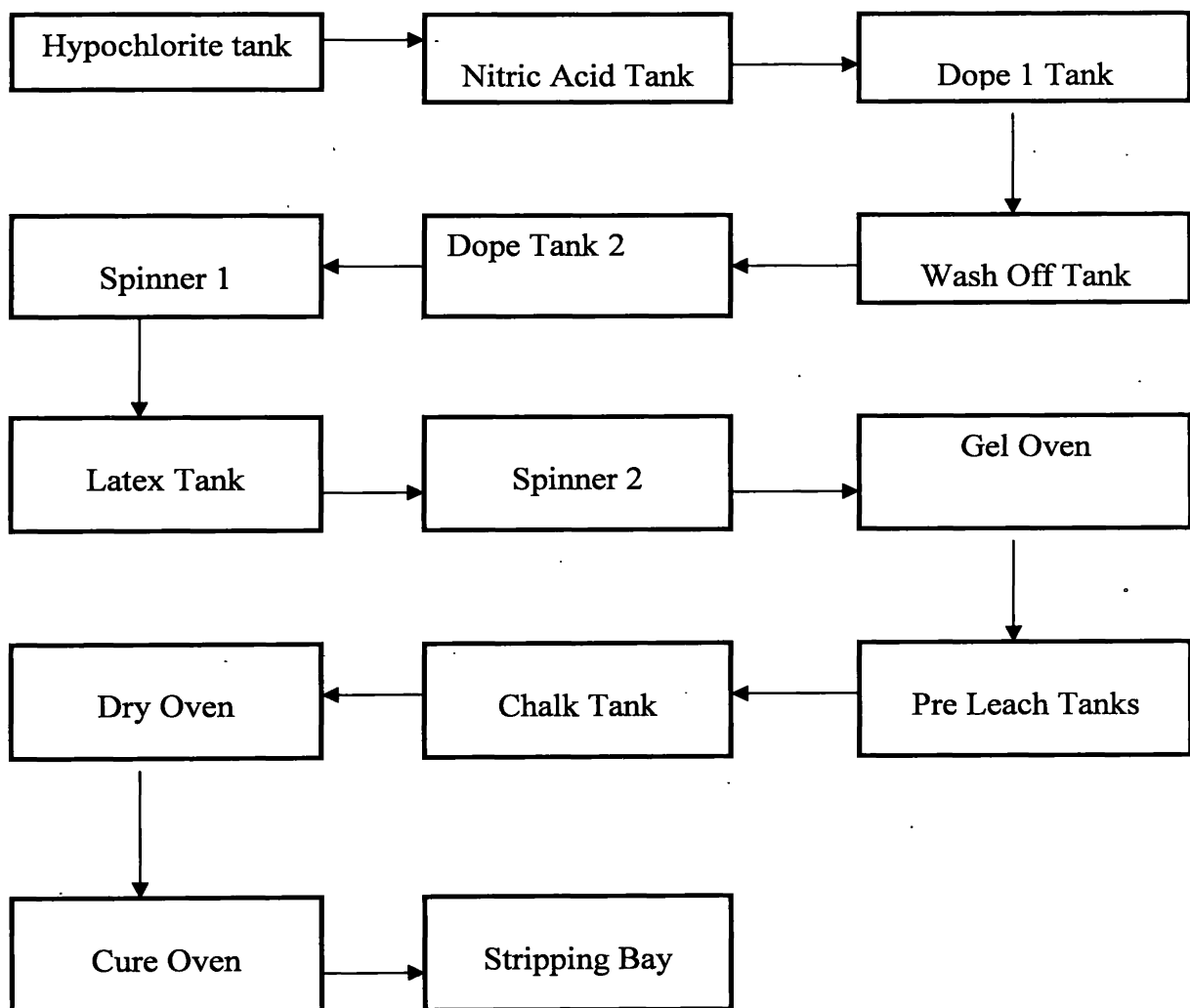


Fig 1.19 Surgical glove production process

2.4 TESTING

Listed below are tests which involved in understanding and precaution about the preparations and compounding are concerned. For this tests are more commonly used.

Which are,

- Particle size test
- TSC (Total Solid Content) test
- TSI (Toluene Swell Index) test
- Tensile Test

2.4.1 Particle size test

Concerning Particle size is an important factor because rubber particle has a size in between 1-10 micro meters. So vulcanizing solid particles should achieve the particle size in between 1-4 micro meter, which they could in cooperate with the rubber particle.

The method is arranged as following,

- Pour 10 ml of distilled water in to a test tube
- Introduce 2 to 3 drops of the dispersion to the water sample
- Investigate the prepared mixture using a microscope with 40x lens resolution and 10 x eye piece resolutions.

2.4.2 TSC test

Total solid content in any mixture is important this governess the thickness of the gloves and required amount of vulcanizing material in the mixture. So in every step TSC is taken necessary in keeping the

TSC is preceded as following,

Take a clean Petri dish and weigh it using a electronic analytical balance. Pour 2.00g of the mixture liquid or dispersion. Dry it in a drying oven keeping the temperature 100°C for about 1hr. Weigh

- again the dried solid with the Petri dish. Calculate the TSC% using the below equation.

(Final weight of the Petri dish with solid material – Initial weight of the Petri dish)

$$\text{TSC \%} = \frac{\text{Initial Sample weight}}{\text{Initial Sample weight}} \times 100 \%$$

2.4.3 TSI test

The stage of the vulcanizing has occurred or approximation of how much cross-linking in between rubber particles is investigated by this method. This is an important measurement to get the idea about pre-vulcanization occurred in a compounded latex mixture and to find the quality of a raw latex.

TSI done as following,

Take a clean thick board with dimensions of 2"x 1" and dip it in to Ca (NO₃)₂ solutions called Diacell solution or dope solution for about 10 sec and take out. Again dip the board in to a raw latex or compounded latex mixture for about 10sec and take out. Keep the latex covered board exposed to air dry or coagulate for about 2 mins. Using a die-cutter (instrument used to cut circular dimensions) cut circles films from the coagulated latex. Place the latex films in a Toluene filled Petri dish and allow for 45 to 60 mins swelling. Measure the diameter of the final swelled latex film and do the following calculation.

$$\text{TSI \%} = \frac{\text{Final Diameter of the latex film – Diameter of the di-cutter}}{\text{Diameter of the di-cutter}} \times 100 \%$$

2.4.4 Tensile Test

This is the final test, done to finished glove product, even after packaging or from the machine. To this there are specified standards as *American Society for Testing and Materials (ASTM)* standards, *European Community of Standards (CEN)*, *Japanese Standards Association (JSA)*, like wise.

Here it will be discussed about ASTM standard, as it is applied during the project, for tensile testing. Equipment used for this test is called the Tensile Testing machine (**Fig 1.20**). Where Dumbbell shape film is cut out from the glove according to ASTM standards, and subjected to the machine for tensile testing. Where tensile strength and elongation break values for the glove is found. Here two ways of physical requirement testing performed to the gloves called as before (un-age) and after accelerated aging.

For the accelerated aging test gloves were subjected to $70 \pm 2^{\circ}\text{C}$ temperatures for about 166 2hrs, then the tensile strength and elongation break values were found by using Tensile Testing machine. For the un-age tensile testing above conditions are not subjected, but tensile strength and elongation break values are found with out aging.



Fig 1.20 Tensile testing Machine

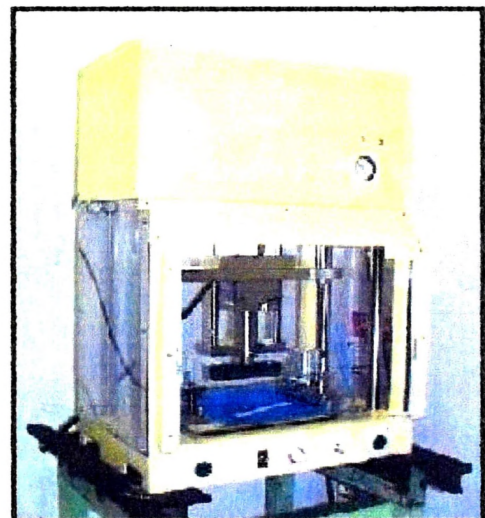


Fig 1.22 Dumbbell cutter

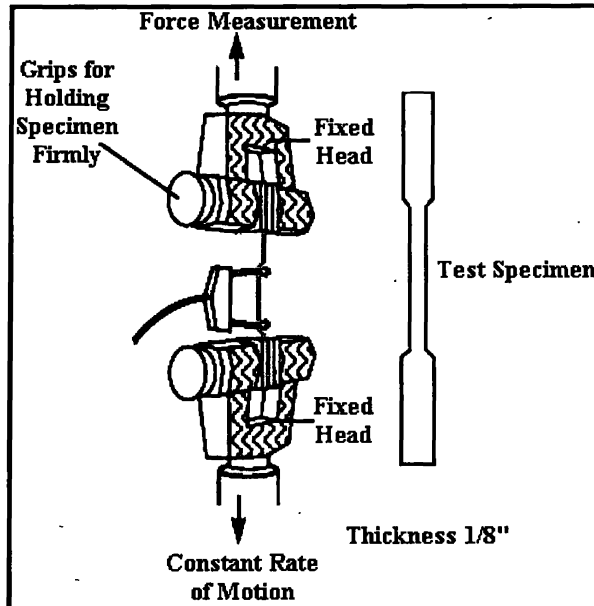


Fig 1.23 Application of Dumbbell to the machine

After Aging		
Type	Tensile Strength	Ultimate Elongation
I	18.0 MPa,min	560%
II	12.0 Mpa,min	490%

Table 1.4 After Aging Tensile Values in ASTM Standards

Before Aging			
Type	Tensile Strength	Ultimate Elongation	Stress at 500% elongation
I	24.0 Mpa,min	750% min	5.5 Mpa ,max
II	17.0 MPa,min	650%,,min	7.0 MPa,max

Table 1.5 Before Aging Tensile Values in ASTM Standards

CHAPTER (03)
MATERIALS AND METHODOLOGY

3.1 Materials used for the mixtures preparation

3.1.1 Vulcanizing dispersion materials:

- Distilled water
- Potassium Hydroxide
- Teepol
- Cellos solution
- Dispersion agent(Vultamol)
- Zinc Oxide
- Sulpher agent
- Thiuram
- ZDEC
- ZDBC

3.1.2 Glove mix preparation materials:

- Low Ammonia Latex
- Oil Emulsion
- Vulcanizing dispersion
- Antioxidant Dispersion
- De-Webber solution

3.2 Equipments used for the procedures

- 7Kg Canisters
- Backers (25 ml to 1000ml)
- Petri Dishes
- Measuring Cylinders
- Electronic analytical balance
- Electric Stirrer
- Ball Mill for the grinding

- Ceramic pebbles
- Thick card Boards (appropriately)
- Oven(temperature range 40oC to 250oC)
- 200 mesh sheets
- Die-Cutter
- Ceramic glove formers
- Glass thermo meter

3.3 Vulcanizing dispersion mixing procedure:

Fill required amount of soft water into the clean 1000 ml Beaker. Switch on the low speed stirrer. Into water add potassium Hydroxide, Teepol and Cellos solution and stir for 2 mins. Switch on the high speed stirrer slowly add Dispersion agent (Vultamol). Stir for 2 mins. Add Zinc Oxide, Sulpher agent, Thiuram, ZDEC and ZDBC slowly in to the canister with 2 mins of stirring intervals. Finally add the remaining water and stir the dispersion for 30 - 40 mins.

Transfer the mixture in to a 2000ml glass bottle together with ceramic pebbles and subject the bottle in to a Ball mill for the grinding for specific particle size.

3.4 Glove mix mixing procedure:

Take Ammonium preserved latex with addition of KOH, Potassium Laureate into a 7kg clean canister and add 70% of oil emulsion to the mixture. Then add the vulcanizing dispersion prepared after 48 hr grinding appropriately into the mixture slowly. To the mixture add Antioxidant dispersion and remaining 30% Oil emulsion in to the mixture.

Allow to stir for 1 hour. Add required amount of heated distilled water at 60°C. Take a TSI reading after every 4 hr, until the TSI comes in between 132% to 135% and if the TSI comes in-between 132% to 135% start the cooling down of mixture by using cool distilled water less than 15°C to keep the mixture temperature between 15°C to 20°C. Check the TSC of the mixture and adjust it to 33% to 37%.

Filter the TSC adjusted compounded latex mixture filter in to another clean 7Kg canister using a 200 mesh and add De-Webber solution prepared by the compounding section into the latex mixture.

Take the compounded latex mixture to the machine for clip-on dipping keeping the temperature of the mixture below 23°C.

3.5 Trial No 1 Preparation of vulcanizing dispersion and Glove mix

3.5.1 Vulcanizing dispersion:

Materials were weight appropriately in beakers as following for the vulcanizing mixture.

Solution introduced	Trial #01
Potassium Hydroxide(20%) Solution	0.74 g
Teepol	0.49 g
Cellos	4.70 g
Dispersion agent(Vultamol)	14.34 g
ZnO	37.58 g
Sulpher agent	34.62 g
Thiuram agent	62.31 g
ZDEC	13.10 g
ZDBC	11.53 g
Distilled Water	281 ml
	total of 450 g

Table 3.1 Vulcanizing dispersion

Then the dispersion mixture or slurry prepared as accordingly to the paragraph 3.3. Ceramic pebbles were introduced to the mixture 2/3 of the total volume of the slurry.

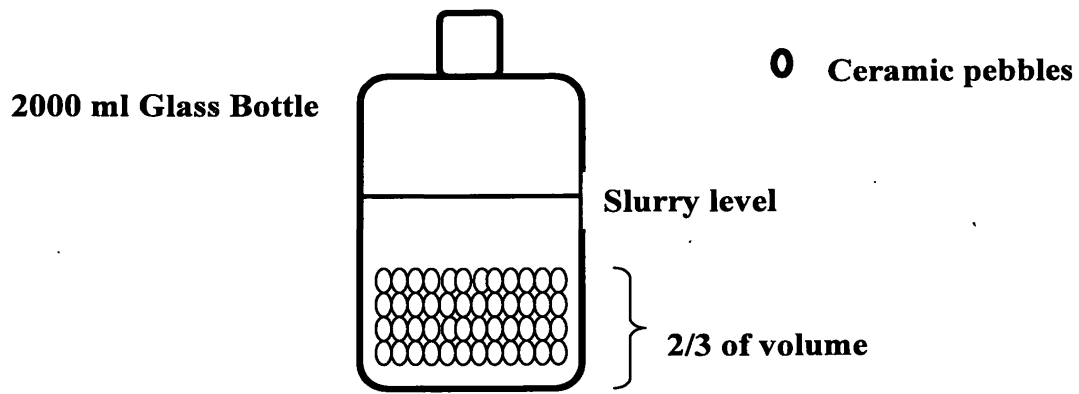


Fig 2.1 Dispersion before ball milling

Using the ball mill the appropriate particle size was achieved, by milling for 48hr of the dispersion.

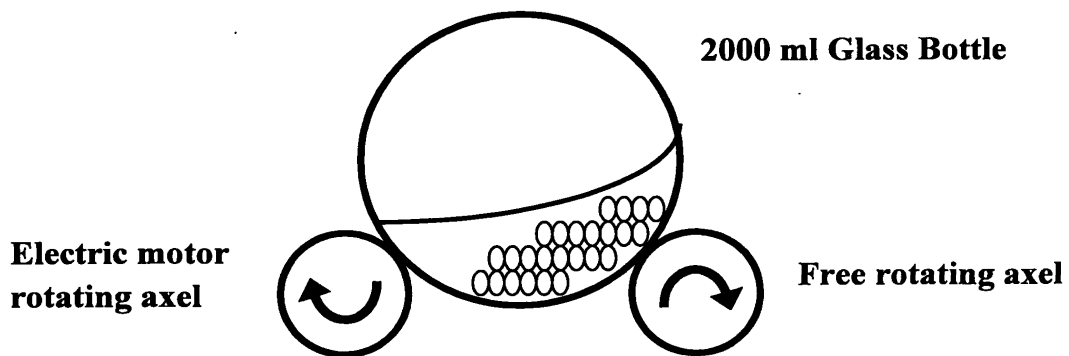


Fig 2.2 Ball Mill Pictorial Illustration

Final appearance of the vulcanizing mixture was creamy, yellowish white, less odor dispersion. Particle size of the dispersion was approximately 2 to 3 micro meters.

3.5.2 Glove mix:

Materials were weight appropriately in to a 7Kg canister as following for the Glove mix.

Dispersions introduced	Trial #01
Low Ammonia Latex (KOH added)	3500 ml
Oil Emulsion	232.53 g
Vulcanizing dispersion	224.65 g
Antioxidant dispersion	38.38 g
Heated Distilled water	1542 ml
Distilled water	610 ml
De-webbing Solution	53.08 g
	total of 6Kg

Table 3.2 Glove mix composition

Here only 224.65g of the dispersion was taken from 450g bulk preparation. The initial TSI of the Stabilized ammonium latex was 173.18%. Were by the addition of KOH the latex is stabilized.

All the ingredients were introduced appropriately as to the paragraph 3.4 in to the mixture with stirring and after all the additions the final TSI was 156.8%. So the stirring was subjected until TSI drops to 134% for about 16 hrs.

After 16hrs the final TSI was 120 % and the cooling on started as accordingly to the paragraph 3.4.

TSC of the cooling on mixture was 38.5 % which was enough for the dipping to start.

Then De-webbing solution was introduced to the mixture and the compounded latex was transferred in to another clean 7Kg canister.

Then the compounded mixture was taken to the machine, by manually(hand) dipping of a former and clipping-on it to the machine for further process of drying and curing of the glove. After the machine trial the trial gloves were stripped off from the former together with normal machine gloves as control.

Some of the trial and control gloves were subjected to the after process. All the after processed and non after processed gloves (both trial and control) were taken to the Tensile testing for the improvement analysis.

3.5.3 Tensile testing:

For tensile testing Tensile Testing Machine was used. Tensile testing was done by un-aging and aging of the gloves. Where un-aging is done by cutting dumbbell shapes using a dumbbell cutter as to ASTM standards values. The aging of the glove were done by applying thermal heat of 70°C for about 7 days in a oven, this is also the same ASTM standard.

3.6 Trial No 2 Preparation of vulcanizing dispersion and Glove mix

This was done same accordingly to the paragraph 3.3, 3.4 and 3.5 procedures. The ingredients were weight as following,

3.6.1 Vulcanizing dispersion mixture:

Solution introduced	Trial #02
Potassium Hydroxide (20%) Solution	0.66 g
Teepol	0.44 g
Cellos	4.18 g
Dispersion agent(Vultamol)	12.75 g
ZnO	33.41 g
Sulpher agent	30.77 g
Thiuram agent	55.38 g
ZDEC	11.65 g
ZDBC	10.33 g
Distilled Water	251 ml
	total of 400g

Table 3.3 Vulcanizing dispersion mixture

As in Trial No 1 the mixture was prepared according to paragraph 3.3 with the same composition and the mixture was subjected to Ball milling for 48 hrs.

3.6.2 Glove mix:

As in trial No 1 the mixture was prepared according to paragraph 3.4 with the same composition into a 7kg canister.

Dispersions introduced	Trial #02
Low Ammonia Latex (KOH added)	3500 ml
Oil Emulsion	232.53 g
Vulcanizing dispersion	224.65 g
Antioxidant dispersion	38.38 g
Heated Distilled water	1542 ml
Distilled water	610 ml
De-webbing Solution	53.08 g
	total of 6Kg

Table 3.4 Glove mix

The TSI of the stabilized latex mixture was 187%. The final TSI before cooling on started, after 16hr of mixing, was 112%. The TSC value was 43.5%, so appropriate adjustment done to the compounded mixture by introducing water until the TSC to ~ 38%.

Here the trial was done in 2 separate ways, one as a machine trial and the other as Lab trial. For the lab trial the drying and curing temperature were dropped by 10oC in each step, but allowing the time as according to machine. Where in the machine Drying and Curing temperatures were 125 °C and 130°C respectively and time kept 1040 seconds. For the lab trial drying and curing temperature kept as 115°C and 120°C respectively and time kept 1040 seconds.

3.6.3 Tensile testing:

For tensile testing Tensile Testing Machine was used. Tensile testing was done for un-aging only to the gloves. Where un-aging is done by cutting dumbbell shapes using a dumbbell cutter as to ASTM standards values. The aging of the glove were done by applying thermal heat of 70°C for about 7 days in a oven, this is also the same ASTM standard.

3.7 Trial No 3 Preparation of vulcanizing dispersion and Glove mix

This trial was done in two separate ways by reducing the addition of ZDBC, according to the ratio ZDEC: ZDBC. Trial no 1 and trial No 2 was done by keeping the ratios of ZDEC: ZDBC as approximately 1:1. Here vulcanizing dispersion was prepared as, ZDEC: ZDBC, 1: 0.75 and 1: 0.50 ratios. All the other preparations and procedures were conducted as accordingly to paragraphs in 3.4, 3.5 and 3.6 procedures. The trials were conducted by doing clipping-on to machine, where drying and curing done in the machine.

3.7.1 75 % ZDBC Vulcanizing dispersion mixture:

In this trial the amount of ZDBC introduced to the Vulcanization disresion is reduced down by 25% than the Trial No 1 and Trial No 2 by keeping the ZDEC as it is.

	Trial #03
Solution introduced	75% ZDBC
Potassium Hydroxide (20%) Solution	0.74 g
Teepol	0.49 g
Cellos	4.70 g
Dispersion agent(Vultamol)	14.34 g
ZnO	37.58 g
Sulpher agent	34.62 g
Thiuram agent	62.31 g
ZDEC	13.10 g
ZDBC	8.63 g
Distilled Water	281 ml
	total of 450 g

Table 3.5 75 % ZDBC Vulcanizing dispersion mixture

3.7.2 Glove mix:

	Trial #03
Dispersions introduced	75% ZDBC
Low Ammonia Latex (KOH added)	3500 ml
Oil Emulsion	232.53 g
Vulcanizing dispersion	224.65 g
Antioxidant dispersion	38.38 g
Heated Distilled water	1542 ml
Distilled water	610 ml
De-webbing Solution	53.08 g
	total of 6Kg

Table 3. Glove Mix

3.7.3 50% ZDBC Vulcanizing dispersion mixture:

This was done same accordingly to the paragraph 3.3 procedure. The ingredients were weight as following for the mixture. Only the ZDBC amount is reduced down to 50 % than the Trial No 1 and Trial No 2.

	Trial #03
Solution introduced	50%ZDBC
Potassium Hydroxide (20%) Solution	0.74 g
Teepol	0.49 g
Cellos	4.70 g
Dispersion agent(Vultamol)	14.34 g
ZnO.	37.58 g
Sulpher agent	34.62 g
Thiuram agent	62.31 g
ZDEC	13.10 g
ZDBC	5.756g
Distilled Water	281 ml
	total of 450 g

Table 3. 50% ZDBC Vulcanizing dispersion mixture

3.7.4 Glove mix:

	Trial #03
Dispersions introduced	50% ZDBC
Low Ammonia Latex (KOH added)	3500 ml
Oil Emulsion	232.53 g
Vulcanizing dispersion	224.65 g
Antioxidant dispersion	38.38 g
Heated Distilled water	1542 ml
Distilled water	610 ml
De-ebbing Solution	53.08 g
	total of 6Kg

Table 3.6 Glove mix

From each trial, control samples were taken from the machine together with trial samples. For some of the samples after process was done, they were named as ex-dryer samples and the others as ex machine (with no after process). This sampling was done to both 75% and 50% ZDBC.

3.7.5 Tensile testing:

For tensile testing Tensile Testing Machine was used. Tensile testing was done only un-aging to the gloves. Where un-aging is done by cutting dumbbell shapes using a dumbbell cutter as to ASTM standards values. The aging of the glove were done by applying thermal heat of 70°C for about 7 days in an oven, this is also the same ASTM standard.

CHAPTER (04)
RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Trial No 1 results :

Particle size of the vulcanization dispersion was in between 2 to 3 micro meters. The Initial TSI value of the stabilized latex was 173.18 %.The TSI value before cooling-on was (114 – 115) %.Final TSC of the glove mix was, 38.35 %.

By the clipping-on to the machine process 5 samples were prepared from the trial glove mix and 10 samples were collected from the machine for control. All of samples were subjected to after process and appropriate tensile testing were conducted as according to ASTM standards for both aging and Un-aging. Below are the tensile results for both methods.

4.1.1.1 Un-age tensile results of Control:

Control UTS(MPa)	Control EB %	Control 500 % modulus
29.377	867.0	2.712
30.429	869.0	2.789
29.825	871.0	2.814
30.605	882.0	2.689
25.705	840.0	2.710
29.188	865.8	2.743

Table 4.1 Trial No.01 Un-age tensile results of Control gloves

4.1.1.2 Un-age results of trial:

Trial UTS(MPa)	Trial EB %	Trial 500 % modulus
29.140	815.0	3.317
32.363	834.0	3.468
26.654	814.0	3.100
32.951	844.0	3.365
30.705	827.0	3.367
30.363	826.8	3.323

Table 4.2 Trial No.01 Un-age tensile results of Trial gloves

4.1.1.3 Age results for control

Control UTS(MPa)	Control EB %	Control 500 % modulus
26.859	834.1	2.585
18.570	760.5	2.592
27.810	878.5	2.314
24.600	844.6	2.355
26.279	808.9	2.784
24.824	825.3	2.526

Table 4.3 Trial No.01 Age tensile results of Control gloves

4.1.1.4 Age results for Trial

Trial UTS(MPa)	Trial EB %	Trial 500 % modulus
21.302	756.9	2.899
19.328	753.9	2.818
21.449	747.8	3.133
19.452	745.9	2.966
21.884	764.5	2.970
20.683	753.8	2.957

Table 4.4 Trial No.01 Age tensile results of Trial gloves

4.1.2 Trial No2 results :

Particle size was kept in-between 2 to 4 micro meters. The Initial TSI value of the stabilized latex was 187%. The TSI value before cooling-on was (112) %. Final TSC of the glove mix was, 43.5%.

So the TSC of the glove mix was adjusted by introducing distilled water as required to drop TSC to 38%.

By the clipping-on to the machine process 3 samples were prepared from the trial glove mix and 6 samples were collected from the machine for control.

Another 3 samples of trial gloves were prepared in the lab by applying the drying and curing in lab scale dropping 10°C from each step, accordingly to the paragraph 3.7.2 procedure.

All of them were subjected to after process and appropriate tensile testing were conducted as according to ASTM standards for Un-aging.

4.1.2.1 Lab Trial tensile results

UTS(MPa)	EB%	500% modulus(MPa)
22.227	747	3.547
23.818	772	3.293
25.597	784	3.196
28.865	832	2.908
29.658	824	3.124
28.577	814	3.245
27.087	799	3.220

Table 4.5 Trial No.02 Un-age tensile results of Lab Trial gloves

4.1.2.2 Machine(M/C) Trial tensile results

UTS(MPa)	EB%	500% modulus(MPa)
29.49	811.0	3.581
29.466	805.0	3.821
30.283	802.0	3.917
29.551	803.0	3.939
25.728	770.0	3.916
25.152	753.0	4.192
29.478	802.5	3.917

Table 4.6 Trial No.02 Un-age tensile results of Machine Trial gloves

4.1.2.3 Control sample tensile results

UTS(MPa)	EB%	500% modulus(MPa)
29.850	830	3.668
29.951	811	3.995
27.740	818	3.442
29.549	824	3.618
30.001	827	3.568
29.850	824	3.618

Table 4.7 Trial No.02 Un-age tensile results of Control gloves

4.1.3 Trial No 3 results:

4.1.3.1 75 % ZDBC Trial

Particle size was kept in-between 2 to 4 micro meters. The Initial TSI value of the stabilized latex was 156%. The TSI value before cooling-on was 94.54% .Final TSC of the glove mix was, 40.5%.

By the clipping-on to the machine process 6 samples were prepared from the trial glove mix and 12 samples were collected from the machine for control.

4 of the trial samples together with 6 of the machine samples were subjected to after process and they we called as Ex-Dryer samples. Remaining 2 trial samples and 6 machine samples were called as Ex-Machine samples.

For both samples appropriate tensile testing were conducted as according to ASTM standards for Un-aging.

4.1.3.1.1 Trial Samples Ex-machine tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
29.541	860.0	29.431	858.0	3.494
28.676	856.0	28.538	855.0	3.386
27.985	840.0	27.87	839.0	3.685
26.396	840.0	26.281	840.0	3.340
27.801	826.0	27.663	824.0	3.916
28.126	846.0	27.993	845.0	3.560
29.260	869.7	29.140	868.0	3.430

Table 4.8 75% ZDBC Un-age tensile results of before after process Trial gloves

4.1.3.1.2 Control Samples Ex-Machine Tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
31.012	942.0	30.874	940.0	2.599
31.975	924.0	31.858	923.0	3.113
31.813	940.0	31.785	940.0	2.764
30.431	920.0	30.321	919.0	3.123
30.956	934.0	30.818	933.0	2.736
26.451	879.0	26.313	878.0	2.985
30.439	923.2	30.328	922.2	2.880

Table 4.9 75% ZDBC Un-age tensile results of before after process control gloves

4.1.3.1.3 Trial Samples Ex-Dryer Tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
29.055	797.0	28.900	796	3.892
26.300	777.0	26.215	776	3.955
26.268	785.0	26.125	784	3.849
27.415	778.0	27.271	777	4.177
25.195	772.0	25.046	772	3.849
26.084	782.0	25.941	781	3.972
30.271	805.0	30.116	804	4.003
28.701	792.0	28.569	791	4.064
28.953	797.0	28.792	796	3.939
27.596	793.0	27.463	792	3.936
24.408	761.0	24.323	760	4.104
23.196	741.0	23.048	740	4.231
24.802	766.5	24.685	766	3.977

Table 4.10 75% ZDBC Un-age tensile results of after processed Trial gloves

4.1.3.1.4 Control Samples Ex-Dryer Tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
30.745	842.0	30.641	841.0	3.395
29.271	833.0	29.166	832.0	3.474
31.785	849.0	31.592	850.0	3.372
33.305	867.0	33.167	866.0	3.233
31.122	803.0	30.983	802.0	4.228
30.624	849.0	30.458	848.0	3.233
32.864	824.0	32.67	822.0	4.008
29.061	834.0	28.877	835.0	3.317
31.088	836.0	31.062	835.0	3.704
32.088	854.0	32.062	854.0	3.475
29.614	820.0	29.509	819.0	3.712
30.193	840.0	30.061	839.0	3.396
30.980	837.6	30.854	836.9	3.546

Table 4.11 75% ZDBC Un-age tensile results of after processed Control gloves

4.1.3.2 50% ZDBC Trial

Particle size was kept in-between 2 to 4 micro meters. The Initial TSI value of the stabilized latex was 193.87%. The TSI value before cooling-on was 131.79%. Final TSC of the glove mix was, 40.8%. So the TSC of the glove mix was adjusted by introducing distilled water as required to drop TSC to 37.3%.

By the clipping-on to the machine process 6 samples were prepared from the trial glove mix and 12 samples were collected from the machine for control.

4 of the trial samples together with 6 of the machine samples were subjected to after process and they we called as Ex-Dryer samples.

Remaining 2 trial samples and 6 machine samples were called as Ex-Machine samples.

For both samples appropriate tensile testing were conducted as according to ASTM standards for Un-aging.

4.1.3.2.1 Trial sample Ex-machine tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
30.266	930.0	30.100	929.0	2.792
29.768	942.0	29.602	940.0	2.736
30.790	943.0	30.680	942.0	2.764
28.165	947.0	28.055	946.0	2.598
28.745	939.0	28.607	937.0	2.625
29.243	934.0	29.105	932.0	2.681
29.490	939.2	29.350	937.7	2.690

Table 4.12 50% ZDBC Un-age tensile results of before after process Trial gloves

4.1.3.2.2 Control sample Ex-machine tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
30.403	932.0	30.265	931.0	2.787
28.515	931.0	28.422	930.0	2.579
29.403	943.0	29.482	942.0	2.487
30.523	925.0	30.403	924.0	2.908
29.081	922.0	28.937	921.0	2.571
30.019	898.0	29.898	896.0	2.980
29.570	929.3	29.430	928.0	2.670

Table 4.13 50% ZDBC Un-age tensile results of before after process Control gloves

4.1.3.2.3 Trial sample Ex-dryer tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
30.160	836.0	30.050	835.0	3.251
30.382	814.0	30.233	847.0	3.295
28.104	814.0	27.971	813.0	3.494
32.814	843.0	32.792	843.0	3.582
29.254	832.0	29.099	831.0	3.273
31.399	825.0	31.266	824.0	3.781
29.475	842.0	29.320	841.0	3.206
30.427	835.0	30.265	833.0	3.363
27.340	817.0	27.225	816.0	3.248
30.404	816.0	30.242	815.0	3.685
29.367	808.0	29.206	807.0	3.570
31.440	842.0	31.302	841.0	3.271
29.311	820.0	29.153	819.0	3.422

Table 4.14 50% ZDBC Un-age tensile results of after processed Trial gloves

4.1.3.2.4 Control sample Ex-dryer tensile results

Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
25.037	8360	24.922	835.0	2.902
31.141	844.0	31.062	843.0	3.448
31.667	853.0	31.535	852.0	3.343
32.693	866.0	32.535	865.0	3.290
29.771	838.0	29.719	837.0	3.316
30.298	848.	30.140	847.0	3.238
29.903	808.0	29.772	807.0	3.975
29.640	847.0	29.456	845.0	3.185
27.192	817.0	27.166	817.0	3.396
28.982	814.0	28.876	813.0	3.738
30.509	837.0	30.430	837.0	3.448
27.482	800.0	27.350	799.0	3.685
29.526	834.0	29.414	833.1	3.414

Table 4.14 50% ZDBC Un-age tensile results of after processed Control gloves

4.2 DISCUSSION

4.2.3 Trial No 1 discussion:

Initially the TSI value of the stabilized latex was 173.18%, because vulcanizing ingredients (curatives) present naturally occurring in latex are very small compared to the bulk rubber volume. So it is not possible to produce glove product from less strengthened vulcanized latex.

To strengthen the glove vulcanizing of the latex by providing cross-linking agent of Sulpher would be effective. So this can be improved by applying thermal energy to the latex together with Sulpher as the cross linker.

For this process to take place high thermal energy should be provided, which is costly. So by providing catalytic action or accelerative action with for vulcanization this barrier could be broken effectively.

So some of the vulcanizing accelerative materials and sulphur vulcanization have been discussed in the chapter 2.0 in detail with the. So by this introduction pre-vulcanization of the rubber particles can be derived with small thermal energy.

The reason for the reduction of TSI down to 115% is the reason of pre-vulcanization. Here the accelerative effect is improved by introducing ZDBC except to ZDEC, which is normally used for the production. This was accounted by comparing the time taken to ready the glove mixture for dipping; normally it takes about nearly 20hr but by introducing the ZDBC this was reduced down to 16hr and less to get the appropriate TSI value for cooling-on to start (procedurally 135% before cooling-on).

Tensile testing is important after the production of gloves, where peak values and break values of a glove are important for the donning. Even the level of vulcanizing can be distinguished by the tensile results of a glove. By vulcanizing, the physical requirement of glove also improves. So the result is somewhat a mirror image for the understanding of the vulcanization level.

By comparing the un-age results of trial and control (4.1.1.1, 4.1.1.2), here introduction of ZDBC was equal to the weight of ZDEC (1:1), the vulcanization has gone up to over vulcanization. Even by the age results (4.1.1.3 and 4.1.1.4) comparison the level that should be kept not exceeding, which proven the over vulcanization of the trial glove.

4.2.3 Trial No 2 discussion:

Initially the TSI value of the stabilized latex was 187%. After the compounding and allowing the latex for 16 hr of stirring the TSI dropped down to 112% before cooling on. By cooling on the thermal effect of the acceleration effect reduces.

The amount of glove samples were not enough to conduct aging tensile test, so only for un-age tensile test done.

The reason for this lab trial is to see if the reduction of temperature would keep the vulcanization not exceeding the normal, and to get the speculated tensile results out from it.

By comparing the tensile result for both machine trail, lab trial and control samples (4.1.2.1, 4.1.2.2 and 4.1.2.3) it is seen that lab trial have less value comparing to the machine produced gloves. This would be the reason of not well curing have taken place in the lab scale oven system. Even hot air blowing rate of a lab scale oven is not equivalent to that of the machine hot air blow.

So this gives rise to less vulcanization than to the normal gloves produced. But the machine produced trial samples have given higher values in all the results that proven the ZDEC: ZDBC 1:1 ratio is not appropriate for the production, which it gives rise to over-vulcanization risk.

4.2.3 Trial No 3 discussion:

In 75% ZDBC,

The amount of ZDBC introduced to the vulcanization dispersion was reduced by 25% than the initial trials. Where keeping the ratio of ZDEC: ZDBC as 1:0.75 in weight. Weights were adjusted as accordingly.

Initially the TSI value of the stabilized latex was %. After the compounding and allowing the latex for 16 hr of stirring the TSI dropped down to % before cooling on. By Cooling on the thermal effect of the acceleration effect reduces.

The tensile test was done to both Ex-Dryer (after processed) and Ex-machine (not after processed) gloves in both trial and control. But

important result considered is the Ex-dryer tensile results. Were they are the finished goods of the production.

By comparing the tensile results (4.1.3.1.3 and 4.1.3.1.4) it shows less values comparing to the control, where the TSC was not reduced down to 38%. So the thickness of the glove have govern this results.

In 50% ZDBC,

The amount of ZDBC introduced to the vulcanizing dispersion was reduced by 50% than the initial trials. Where keeping the ratio of ZDEC: ZDBC as 1:0.50 in weight. So the weights introduced were adjusted as accordingly.

Initially the TSI value of the glove mix was 193.87%. After allowing for 16hr it dropped only to 131.79%, which is nearly to the speculated value for cooling-on to start. So this concludes that the amount of ZDBC keeps in the necessary value.

Here also only the tensile results for ex-dryer concerned to get an idea about the finished product. By comparing the control and trial sample tensile values (4.1.3.2.3 and 4.1.3.2.4), which goes nearly parallel to the control values, giving the idea of safe production can be carried out with this introduction.

CHAPTER (05)

CONCLUSION

5.1 Conclusion

Naturally rubber contains very less amount of curatives present in them, which is not appropriate for to achieve a good quality product. so to solve this problem vulcanizing agent such as sulphur can be introduce to the rubber mixture, where by forming cross-links in between polymeric rubber particles. By vulcanizing the physical appearance of the product improves. For this to take place higher thermal energy should be introduced to the mixture, which is some what expensive method to follow. So to overcome this catalytic action performing ingredients so called accelerators are introduced for the mixture with lesser thermal introduction. ZDEC and ZDBC are some of the accelerators that are available commercially. ZDBC is more active than the ZDEC.

For the production of gloves the physical appearance is very much concerned to have donning improved glove products, to have improved tensile strength of the glove. This is facilitated by the vulcanizing or curing.

Project was arranged around a usual glove product in Ansell, where to have optimum formulation for the glove product to improve the pre-vulcanizing within the glove mix. For this 3 ways of trials were carried out to find the optimum formulation.

For this final tensile testing performed both in aging and un-aging to the trial manufactured glove products as according to ASTM standers. Where tensile strength governs the idea about improvement of the pre-vulcanizations and curing of the glove.

By comparing the Trial No 01 and Trial No 02 machine trials (**Appendix I** and **Appendix II**) it is visual that by keeping the ZDEC: ZDBC as 1:1 arises a risk of

over vulcanization, by reduction of the weight amount applied would give a safer vulcanization to the glove. So the 3rd trial arises as according to this situation.

3rd trial was carried out by reducing of ZDBC respectively as 25% and 50%, from the weight introduced to the vulcanization dispersion. Here only the Ex-dryer results are important to get an idea for the formulation arrangement. By comparing the tensile results (**Appendix III** and **Appendix IV**) where the 50% reduction go more equally with control values, so this gives out an idea that by keeping the level of ZDBC introduction in-between 50 % and 75% would give a safer vulcanizing level of optimum formulation for curing.

5.2 Further Studies

For further studies, compounding a vulcanizing dispersion with the reduced ZDBC level by 40% weight and carrying performing a machine trial with reduced temperature of drying and curing oven.

Keeping the ZDBC level reduced to 40% than the initial and reducing the temperature of adding hot water to the mixture or speeding up the process than the usual(because of TSI reduction occur faster).

Replacing ZDEC by ZDBC, totally with equal amount or reducing by 25% according to ZDEC weight and performing the machine trials with reduced temperature of the machine system.

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Trial # 01 – ZDEC : ZDBC =1:1

Un-age tensile test

Control Sample (CS)			Trial Sample(TS)		
CS UTS(MPa)	CS EB %	CS 500 % modulus	TS UTS(MPa)	TS EB %	TS 500 % modulus
29.377	867.0	2.712	29.140	815.0	3.317
30.429	869.9	2.789	32.363	834.0	3.468
29.825	871.0	2.814	26.654	814.0	3.100
30.605	882.0	2.689	32.951	844.0	3.365
25.705	840.0	2.710	30.705	827.0	3.367
29.188	865.8	2.742	30.363	826.8	3.323

Age tensile test

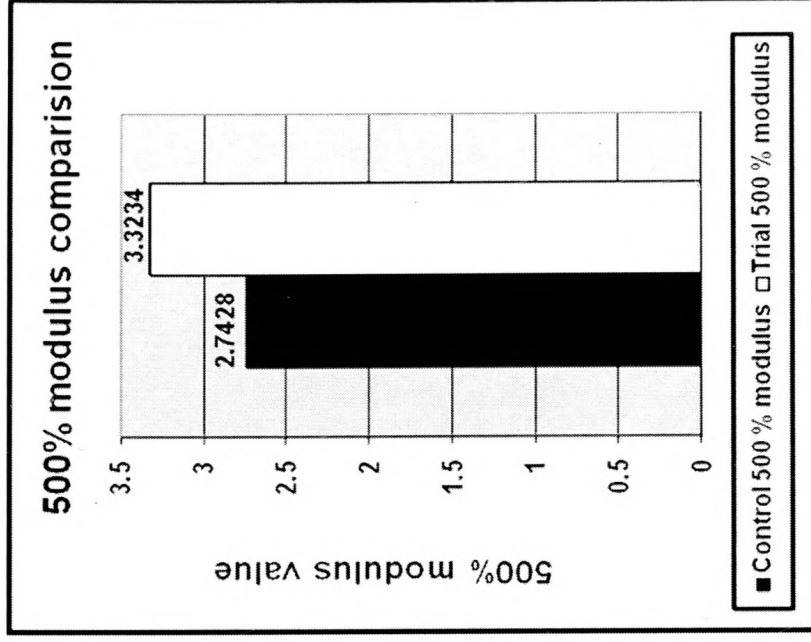
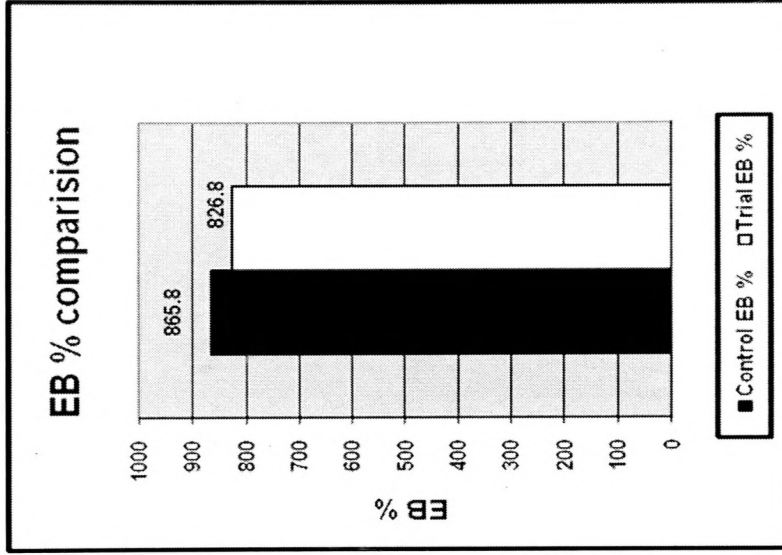
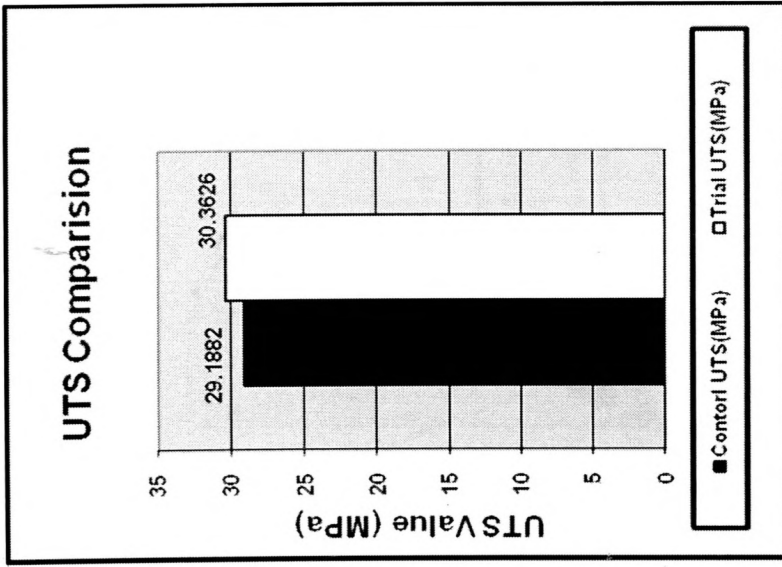
Control Sample (CS)			Trial Sample(TS)		
CS UTS(MPa)	CS EB %	CS 500 % modulus	TS UTS(MPa)	TS EB %	TS 500 % modulus
26.859	834.1	2.585	21.302	756.9	2.899
18.570	760.5	2.592	19.328	753.9	2.818
27.810	878.5	2.314	21.449	747.8	3.133
24.600	844.6	2.355	19.452	745.9	2.966
26.279	808.9	2.784	21.884	764.5	2.970
24.824	825.3	2.526	20.683	753.8	2.9572

** Both test were carried out under ASTM standards.

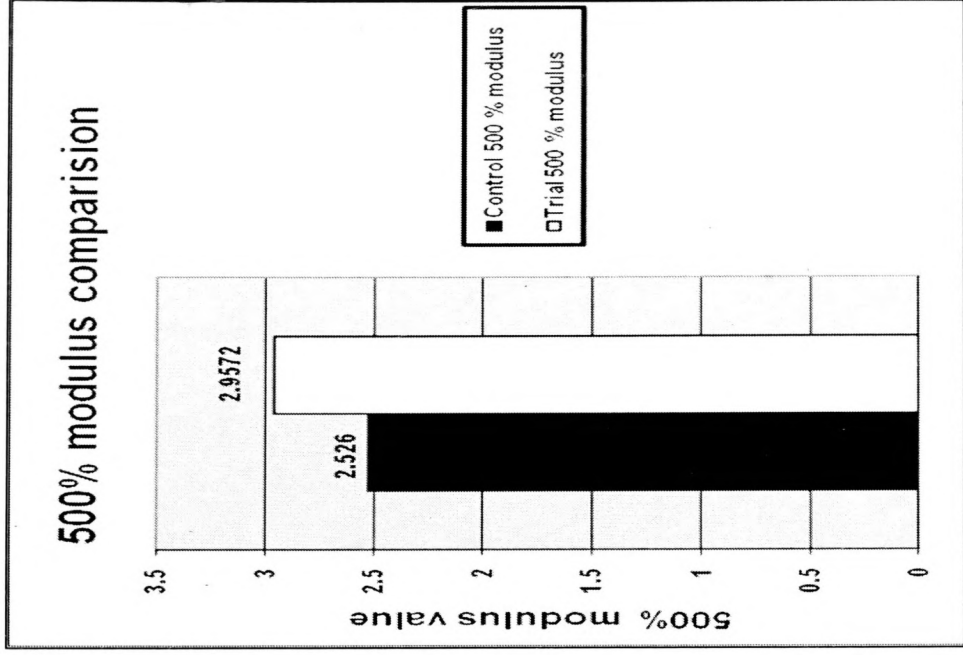
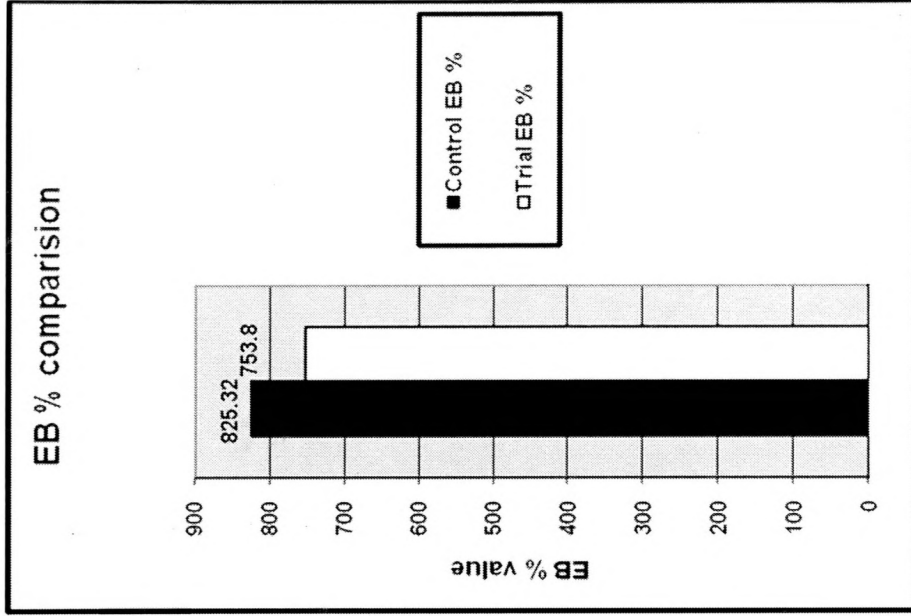
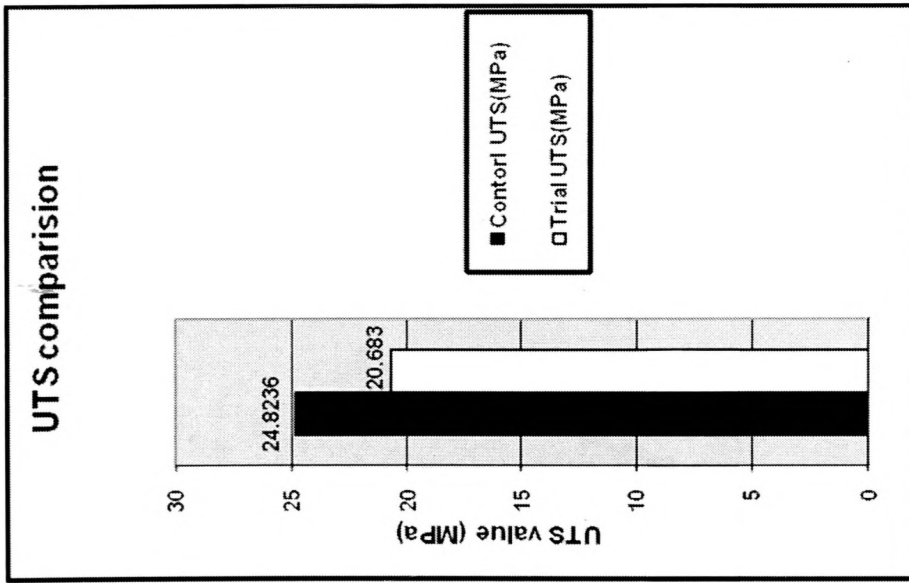
UTS - Ultimate Tensile Test

EB - Elongation Break

Un-age Tensile Comparison



Age Tensile Comparison



APPENDIX II

Trial # 02 with ZDBC introduction & reducing the drying, curing temperatures

Control sample UTS(MPa)	Control sample EB%	Control sample 500% modulus(MPa)
29.850	830.0	3.668
29.951	811.0	3.995
27.740	818.0	3.442
29.549	824.0	3.618
30.001	827.0	3.568
29.850	824.0	3.618

* All the results were taken only at un-age condition.

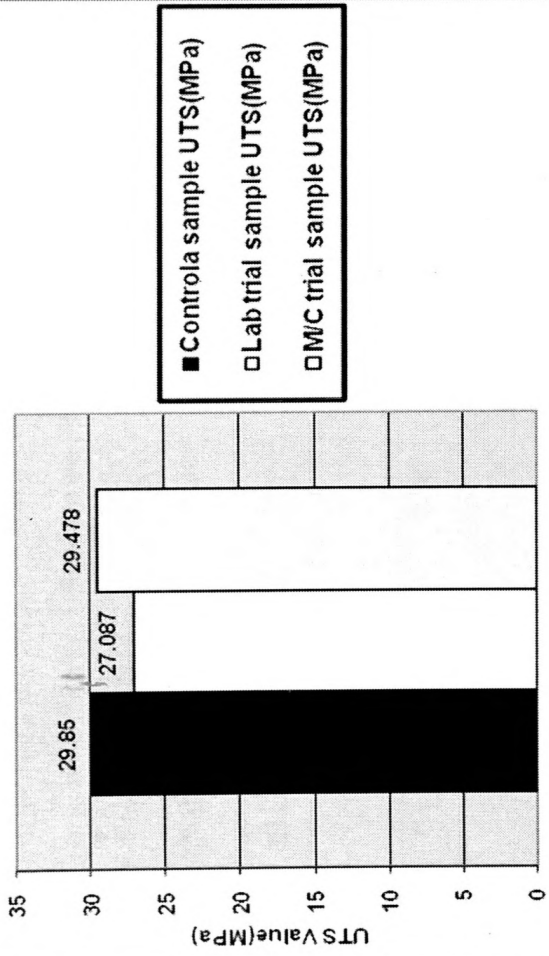
** The drying & curing temperature at lab scale was 105 ° C to 115 ° C for 1hr 10min time (Lab trial samples).

*** Test was carried out for ASTM standards.

Lab trial sample UTS(MPa)	Lab trial sample EB%	Lab trial sample 500% modulus(MPa)
22.227	747.0	3.547
23.818	772.0	3.293
25.597	784.0	3.196
28.865	832.0	2.908
29.658	824.0	3.124
28.577	814.0	3.245
27.087	799.0	3.220

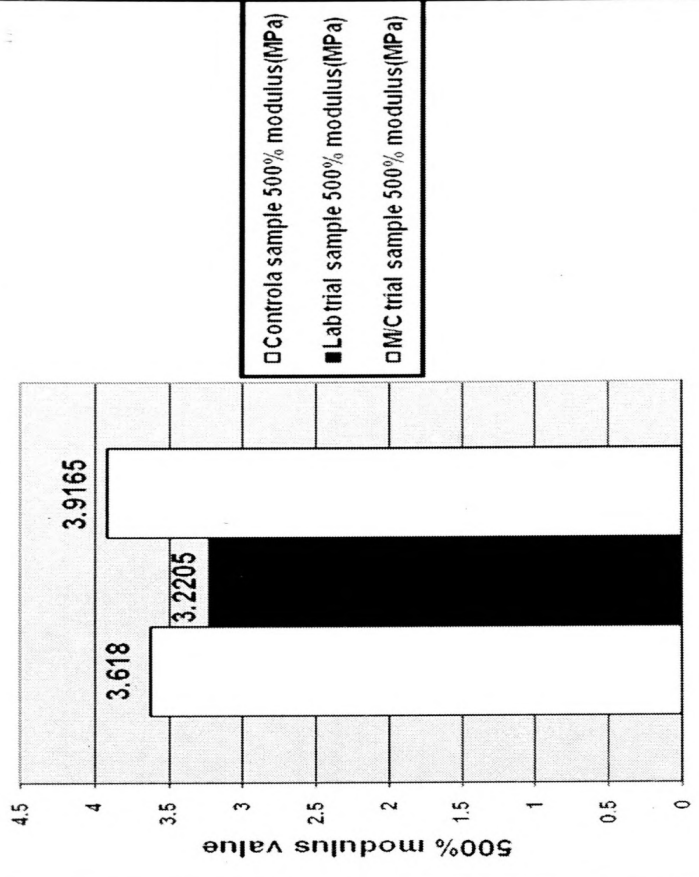
M/C trial sample UTS(MPa)	M/C trial sample EB%	M/C trial sample 500% modulus(MPa)
29.490	811.0	3.581
29.466	805.0	3.821
30.283	802.0	3.917
29.551	803.0	3.939
25.728	770.0	3.916
25.152	753.0	4.192
29.478	802.5	3.917

UTS comparison



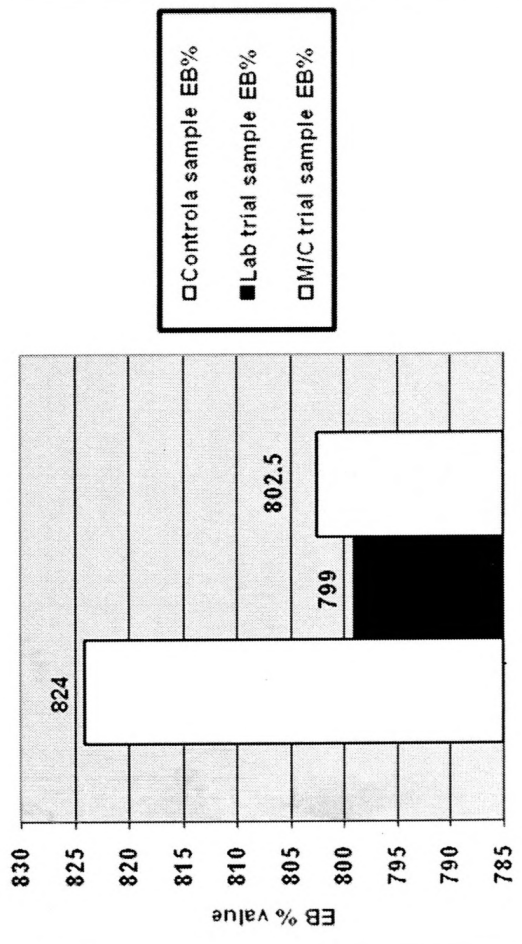
- Control sample UTS (MPa)
- Lab trial sample UTS (MPa)
- MIC trial sample UTS (MPa)

500% modulus comparison



- Control sample 500% modulus (MPa)
- Lab trial sample 500% modulus (MPa)
- MIC trial sample 500% modulus (MPa)

EB % comparison



- Control sample EB %
- Lab trial sample EB %
- MIC trial sample EB %

APPENDIX III

Trial # 03 75% ZDBC introduction—Ex M/C results

	Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulas
A [TSC - 40.8%]	29.541	860.0	29.431	858.0	3.494
Average	28.676	856.0	28.538	855.0	3.386
	29.109	858.0	28.984	856.5	3.440
B [TSC - 38.5%]	27.985	840.0	27.870	839.0	3.685
Average	26.396	840.0	26.281	840.0	3.340
	27.191	840.0	27.076	839.5	3.513
O [TSC - 38.5%]	27.801	826.0	27.663	824.0	3.916
Average	28.126	846.0	27.993	845.0	3.560
	27.964	836.0	27.828	834.5	3.738
Trial Average	28.088	844.667	27.963	843.5	3.564

Control	31.012	942.0	30.874	940.0	2.599
	31.975	924.0	31.858	923.0	3.113
	31.813	940.0	31.785	940.0	2.764
	30.431	920.0	30.321	919.0	3.123
	30.956	934.0	30.818	933.0	2.736
	26.451	879.0	26.313	878.0	2.985
Control Average	30.440	923.2	30.329	922.2	2.887

Trial # 03 50% ZDBC introduction—Ex M/C results

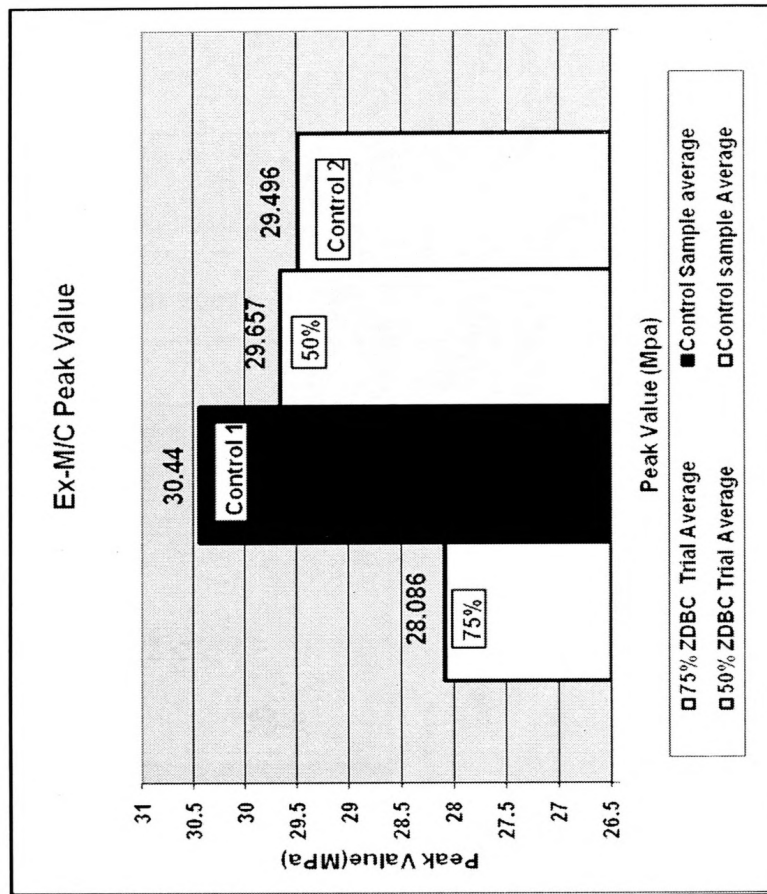
	Peak Value (Mpa)	Peak Value %	Break Value (Mpa)	Break Value %	500% modulus
A ₂	30.403	932.0	30.265	931.0	2.787
	28.515	931.0	28.422	930.0	2.579
Average	29.459	931.5	29.344	930.5	2.683
B ₂	29.403	943.0	29.482	942.0	2.487
	30.523	925.0	30.403	924.0	2.908
Average	29.963	934.0	29.943	933.0	2.698
O ₂	29.081	922.0	28.937	921.0	2.571
	30.019	898.0	29.898	896.0	2.980
Average	29.550	910.0	29.418	908.5	2.776

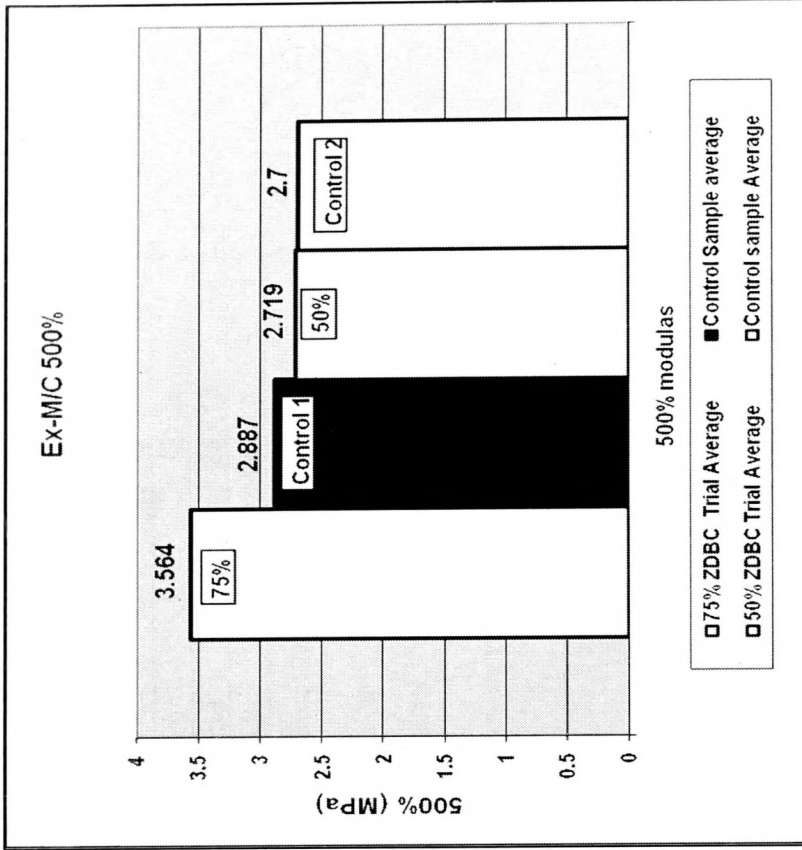
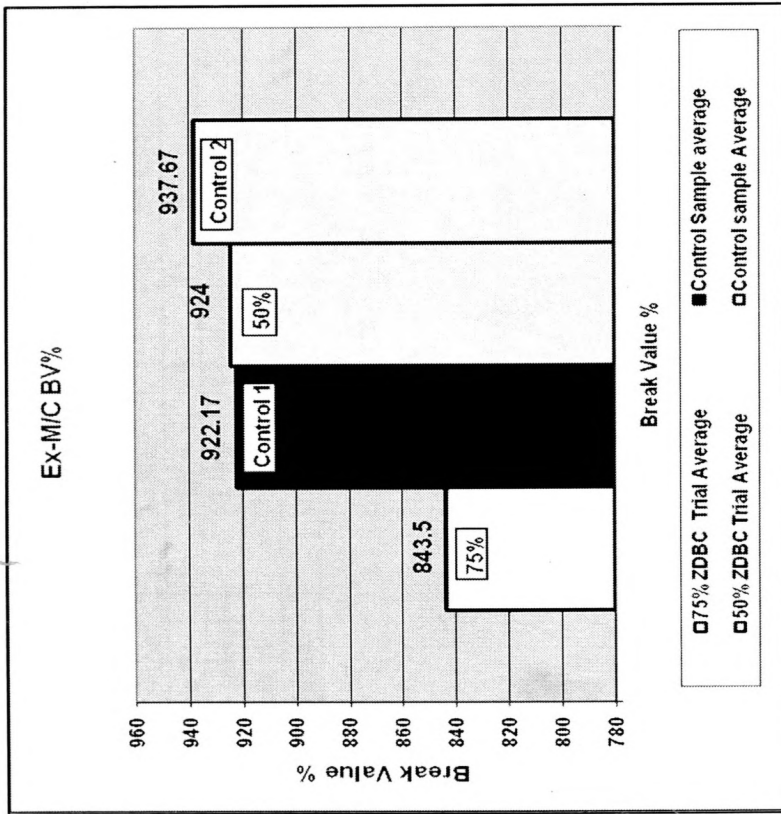
Trial Average	29.657	925.167	29.568	924.0	2.719
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Control ₂	30.266	930.0	30.100	929.0	2.792
	29.768	942.0	29.602	940.0	2.736
	30.790	943.0	30.680	942.0	2.764
	28.165	947.0	28.055	946.0	2.598
	28.745	939.0	28.607	937.0	2.625
	29.243	934.0	29.105	932.0	2.681
Control Average	29.497	939.2	29.359	937.7	2.699

Trial # 03 ZDBC introduction—Ex M/C results compression

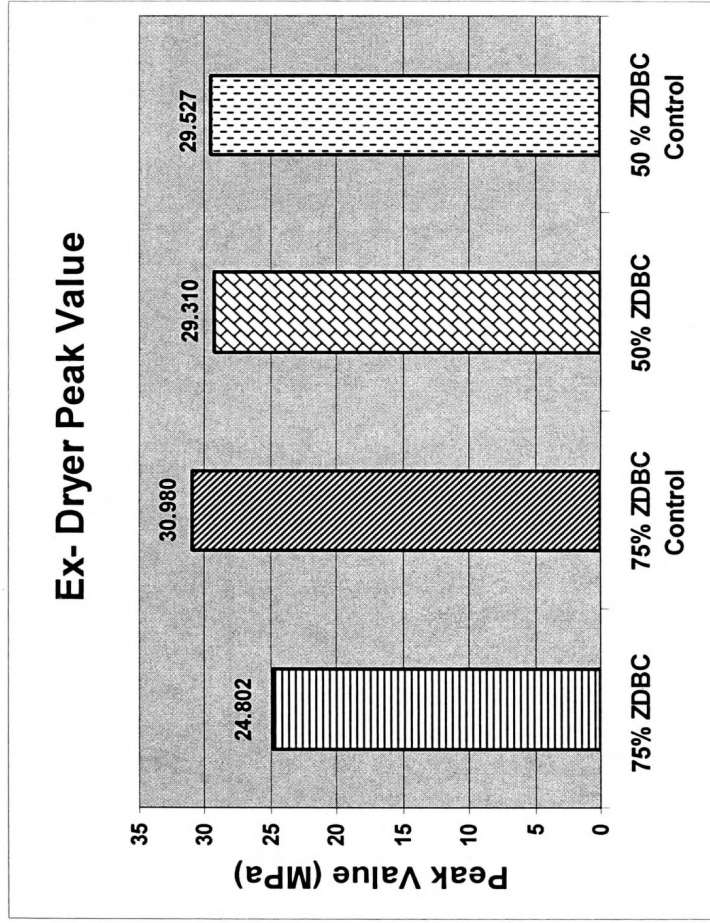
Test Result	75% ZDBC		50% ZDBC	
	Trial Average	Control Sample average	Trial Average	Control sample Average
Peak Value (Mpa)	28.086	30.440	29.657	29.496
Peak Value %	844.7	923.2	925.2	939.2
Break Value (Mpa)	27.963	30.328	29.568	29.358
Break Value %	843.5	922.2	924.0	937.7
500% modulus	3.564	2.887	2.719	2.700

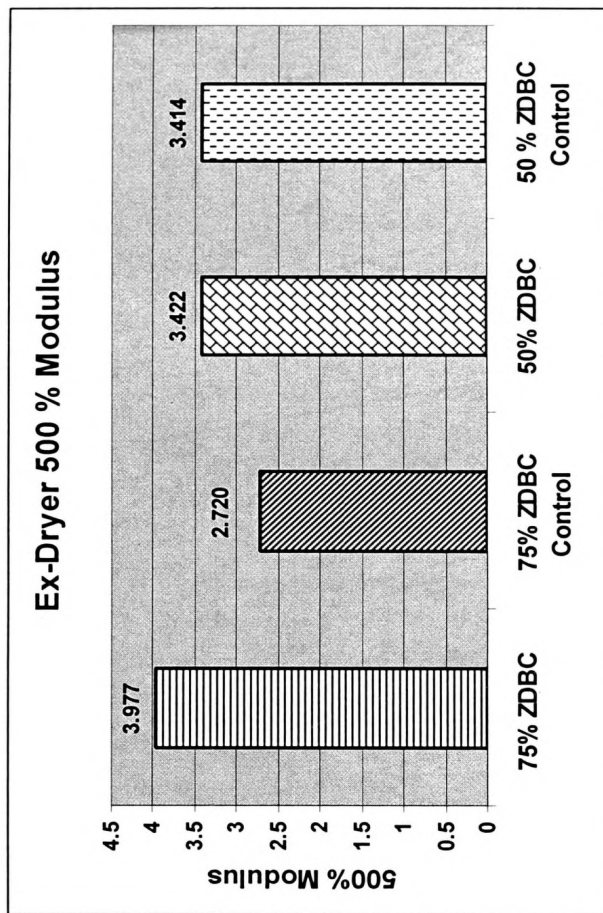
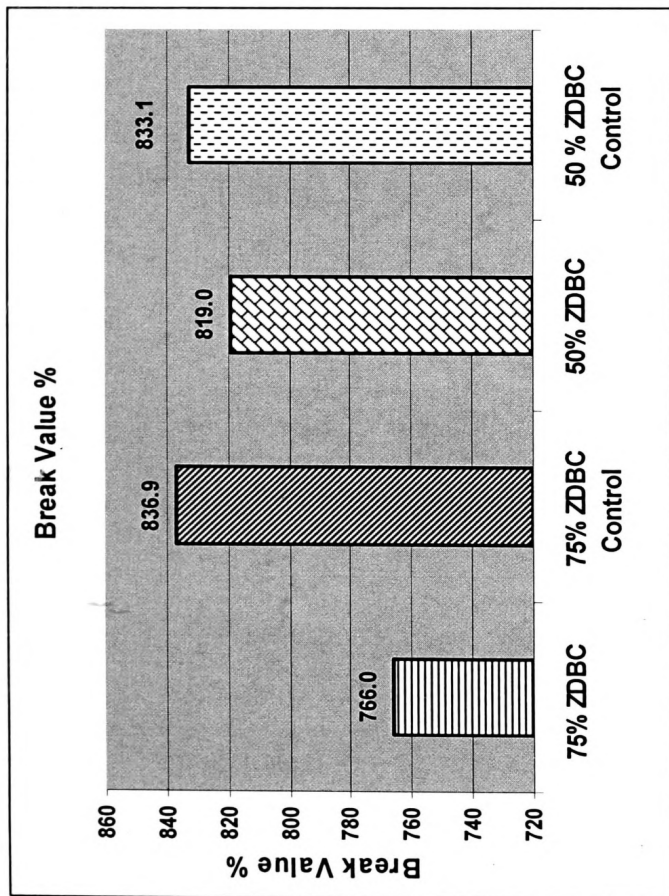




Trial # 03 -Ex Dryer results compression

Test Result	75% ZDBC		50% ZDBC	
	Trial Average	Control Sample average	Trial Average	Control sample Average
Peak Value (Mpa)	24.802	30.980	29.310	29.526
Peak Value %	766.5	837.6	820.0	834.0
Break Value (Mpa)	24.685	30.854	29.153	29.414
Break Value %	766.0	836.9	819.0	833.1
500% modulus	3.977	2.720	3.422	3.414





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