EFFECT OF CHEMICALS AND PROCESS VARIABLES ON NATURAL RUBBER MASTERBATCH

MR.WASON JAITRONGKLA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE
MASTER OF SCIENCE PROGRAMME IN APPLIED CHEMISTRY
SCHOOL OF GRADUATE STUDIES
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
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หัวข้อวิทยานิพนธ์ อิทธิพลของสารเคมีและตัวแปรในกระบวนการผลิตต่อยางธรรมชาติมาสเตอร์แบทช์
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พ.ศ. 2539

บทคัดย่อ

การศึกษาอิทธิพลของสารเคมี และตัวแปรในขบวนการผลิต ที่มีต่อสีมาสเตอร์แบทช์ สำหรับใช้ผสมในยางธรรมชาติ ซึ่งผลิตภัณฑ์ยางธรรมชาติ 2 ชนิดที่นำมาศึกษาคือ พื้นรองเท้า และยางรัดของ

การเตรียมตัวอย่างสำหรับทำการศึกษา จะทำการเตรียมโดยเปลี่ยนแปลงค่าตัวแปรต่างๆ คือ อุณหภูมิของการผสมยาง ความเข้มข้นของสี เวลาในการขึ้นรูป อุณหภูมิการขึ้นรูป และความหนาแน่นของพันธะเครือข่าย โดยใช้สีจำนวน 8 ตัวอย่างมาทำการเตรียมแต่ละตัวแปรดังกล่าวข้างต้น นำตัวอย่างที่เตรียมได้มาทำการวัดค่าความแตกต่างของสีเทียบกับตัวอย่างมาตรฐาน ด้วยเครื่องวัดสี ICS Texicon Colour System แล้วนำค่าความแตกต่างของสี มาทำการวิเคราะห์ถึงผลของตัวแปรแต่ละตัว

อิทธิพลของสารเคมีได้ทำการศึกษาโดยใช้วิธีการ FT-IR และ FT-Raman Spectroscopy

จากการศึกษาพบว่าอุณหภูมิของการผสมยางเป็นตัวแปรหลักที่ทำให้เกิดการเปลี่ยนแปลงของสี และการใช้อุณหภูมิการผสมที่สูงยังมีผลต่อการกระจายตัวของสีอีกด้วย

จากผลของตัวแปรต่างๆ ที่ได้ จะนำมาวิเคราะห์ และเสนอแนะ สำหรับการผลิตเพื่อให้ได้ผลิตภัณฑ์ยางธรรมชาติให้ได้สีสันมีค่าความแตกต่างอยู่ในตามช่วงที่ ยอมรับได้

Thesis Title	Effect of Chemicals and Process Variables on Natural Rubber Masterbatch
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Abstract

This work was developed to study the effect of chemicals and process variables on colouring of rubber products. Two types of rubber product (shoe sole and rubber band) were used for this study.

The samples were prepared by varying factors such as mixing temperature, colour masterbatch concentration, cure temperature, cure time and crosslink density. There are eight colour masterbatches which used in this investigation. Then the colour difference was measured comparable between standard and sample by ICS-Texicon Colour System.

The effect of chemicals interaction were also studied by FT-IR and FT-Raman spectroscopy.

It was found that the mixing temperature was a major effect of colour fading. The high mixing temperature can also effect to the dispersion of pigments.

The effect of each parameters are discussed and referred to processing rubber colour within accepted colour difference.

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Wason Jaitrongkla

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Chapter 1

Introduction

Coloured Rubber Products

Successful utilisation of elastomers requires an understanding of factors which affects to rubber products and properties, i.e. physical and mechanical properties. The factors which govern the mechanical properties such as tensile strength, modulus, elongation, dynamic mechanical properties, etc. of rubber products have been studied and subsequent of published papers can be found. However, physical properties of rubber products are also very interesting such as thermal properties, electrical properties and optical properties which, particularly, involved colouring of the products are still not well understood.

Generally, colouration can be achieved by adding pigments or dyestuffs to rubber compounds. However, solubility of these pigments are limited. Thus, an alteration in corporating them into the rubber can be done via masterbatch process which allows a well dispersion of the dyestuffs. Where a masterbatch is used, the proportion of ingredients in the masterbatch recipe may :

a) be the same as the compound recipe but without curative

b) contain only rubber, fillers, and some softness

c) be richer in filler than the final compound.

Each type of masterbatch will be capable of improving its colouration and colour dispersion which depend upon certain parameters or in combination of each parameters.

The present investigation will observe the discolouration of colour masterbatch in shoe sole and elastic rubber band formulation due to the parameters as follows :-

1. mixing temperature
2. concentration of masterbatch
3. cure temperature
4. cure time (under cure and over cure).

The effect of the these parameters to pigment dispersion and the hardness of coloured rubber products are also studied.

Advantages

1. Explain the factors which strongly influence the colouring of rubber products from the analysis. Thus, plotted data which explain significant parameters can be obtained and may lead to mechanisms of discolouring as well.

2. The effect of the property relationships can be developed from the plots which provide a well define property to corresponding factors.

3. Enable to achieve a good quality control and consistency of rubber products.

Scope of this study

This study can be done by collecting data from the ,experiment and analyses these data. The steps of the experiment are as follows.

1. Design of the equipment and prepare raw materials.

2. Processing of rubber compounds with vary mixing temperatures and concentrations of NR masterbatch in a typical rubber formulation i.e.,

    2.1 Shoe sole formulation

    2.2 Elastic rubber band formulation

3. Prepare vulcanised sheets in different parameters, for example, cure temperature, masterbatch concentration, cure time.

4. Measure properties of vulcanised sheets which compared to standard samples by ICS-Texicon colour system, Durometer Shore A, Scanning Electron Microscope (SEM).

5. Conclusion and discussion parameters which affected to colour strength.

Standard Terminology and Abbreviations

Accelerator a compounding material used in small amounts with a vulcanizing agent to increase the speed of vulcanization.

Antioxidant compounding material used to retard deterioration caused by oxidation.

CBS N-cyclohexyl-2-benzothiazole sulfenamide

Crosslink chemical bond bridging one polymer chain to another. Cure or vulcanisation is an irreversible process during which a rubber compound, through a change in its chemical structure (for example, cross-linking),becomes less plastic and more resistant to swelling by organic liquids while elastic properties are conferred, improved, or extended over a greater range of temperature.

Dispersion (the act of) application of shearing forces to distribute one or more compounding materials uniformly throughout the mass of a continuum material.

Internal mixer a machine with a closed cavity in which a specially shaped rotor (or rotors) masticate the rubber or incorporate and disperse compounding materials, or both, into the rubber.

Masterbatch a homogeneous mixture of rubber and one or more material in known proportions for use as a raw material in the preparation of the final compounds.

Mastication a breakdown or softening of raw rubber, or a mix by the combined action of mechanical work (shear) and atmospheric oxygen, sometimes accelerated by the use of a peptizer and frequently at elevated temperatures.

MBTS benzothiazyl disulfide

Natural rubber (NR) a cis-1,4-polyisoprene that is obtained from botanical source, usually Hevea brasiliensis.

phr part per hundred rubber

PVI pre-vulcanization inhibitor

TMTD tetramethylthiuram disulfide

TMTM tetramethylthiuram monosulfide

Chapter 2

Theory

Rubber Colour Masterbatch

Masterbatch is a homogeneous mixture of rubber and one or more materials in known proportions for using as a raw material in the preparation of the final compounds. Masterbatch is used to facilitate processing or to enhance the properties of the final product, or both. One of the most important masterbatch is the colour masterbatch in which rubber and colourants (dyes or pigments) are mixed.

Colourants

The production of a coloured product, whether rubber, plastic, paper, textile, etc. is generally accomplished by the use of colourants, either dyes or pigments.

Dyes are colourants soluble in at least one of the common solvents, such as water, alcohol or oil. Pigments do not have any significant solvency in such media so that they are described as insoluble. There are two groups of pigments : inorganic and organic pigments. The most common organic pigments are carbon black, phthalocyanines, mono and disazo compounds, quinacridones, indolines, and perylenes. Inorganic pigments (salts and oxides of metals) are generally temperature resistant and readily dispersed, and they have good tinting strength and hiding power. The most widely used of these is titanium dioxide. Other inorganic colourants include iron oxides, cadmium, lead, zinc, mercury, strontium, and barium salts.

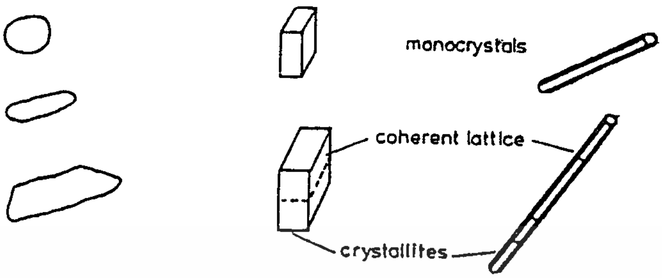
Special colourants are used to produce special effects including fluorescents, metallics, phosphorescents and pearescents. Fluorescents, also called optical brighteners, are all dyes which are the derivatives of stilbene and coumarin. Phosphorescents are inorganic usually comprised of zinc cadmium sulfide or strontium sulfide.

Colourants are available in a wide variety of physical forms. Dry pigments, with which the processor blends the resin directly preceding processing, account for only a small portion of colourants. Predispersed colourant, such as a rubber colour masterbatch or a plasticizer paste is used for ease in blending and processing.

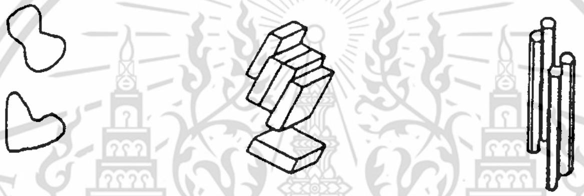
Pigment

The term pigment is linked with a specific particle size range 0.01 to 1 μm, which differs from product to product and during production is capable of being influenced within certain limits. In the definition of pigment particles, a distinction is made between primary particles or single particles, aggregates and agglomerates (Fig. 1)

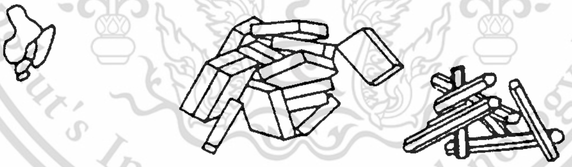
Fig. 1



Primary particles



Aggregates



Agglomerates

Elements of a pigment (R.Gacher and H.Muller 1987:472)

Because of their extremely small particle sizes, primary particles such as those usually obtained during production, exhibit a pronounced tendency to combine. This massing together in a single plane results in the primary particles forming aggregates, which thus possess smaller surface than that corresponding to the sum of the surfaces of their primary particles. The massing together of primary particles and/or aggregates at their corners and edges results in the formation of agglomerates.

Two groups of pigments are inorganic and organic pigments :-

1. Inorganic colour pigment

They are generally characterized by their complete insolubility in plastics and rubbers. Their thermal stability may be high, but this is not neccessarily always true.

1.1 Oxidic colour pigments

If the metal are present in their oxides at the highest valence state, the corresponding pigments have very high thermal stability, since no further oxidation is possible. If metal are present in pigments at a low stage of oxidation, e.g. bivalent iron in standard iron oxide black and brown, the thermal stability of such pigments is limited.

1.2 Pigments with hydroxyl content

Iron oxide yellow, $Fe_2O_3.xH_2O$, $FeO(OH)$ when x=1 , is an oxide-hydroxide of trivalent iron; the possible elimination of water is the reason why its thermal stability is not always adequate.

1.3 Sulfidic pigments

Since hydrogen sulfide is a weak acid, the acid resistance of sulfidic pigments is low. Some products can oxidize under the influence of atmospheric oxygen, thus forming sulfates and undergoing colouristic changes.

1.4 Chromates

Lead chromate exists in three different crystalline forms, of which the monoclinic and the rhombic are yellow and the form presumed to be tetragonal is red. Chrome yellow, $PbCrO_4$ is monoclinic crystalline form of lead chromate, stable at normal temperature. Under the influence of light, lead chromates tend to change their colour towards the dark, green direction. This can be prevented by different forms of surface treatment.

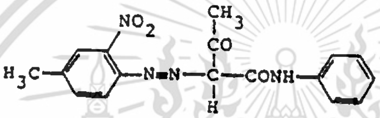
2. Organic colour pigments

Organic pigments are mainly used when brilliance high tinctorial strength and transparency are of decisive importance in a given application. The degree of solubility of an organic pigment is, among other things, dependent on the type of substituents of the base molecule and on the molecular weight of the colourant to the extent that solubility drop as molecular weight increases.

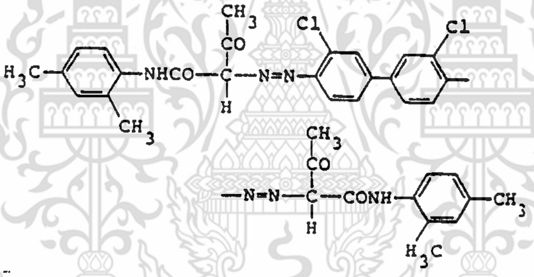
2.1 Azo pigments

Characteristic of this largest class of compounds is the azo (-N=N-) group. A distinction is made between monoazo pigments, which contains only one azo group, disazo pigments, containing two azo groups, disazo condensation pigments, manufactured by a special process, and salts of azo colour acids (colour lakes). The fastness properties of azo pigments differ greatly and range from medium to very high value. The benzimidazolone and disazo condensation pigments can be mentioned as examples of the latter. With the exception of colour lakes, chemical resistance is very good, since readily saponifiable groups are absent. The colour scale ranges from greenish yellow to dark bordeaux. Yellow azo pigments generally contain the acetoacetanilide group, the red pigments the naphthol group. Examples of structures are shown in figures 2 and 3.

Fig. 2

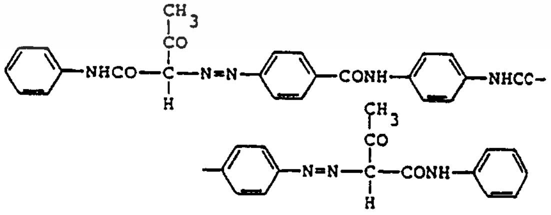


Monoazo pigment

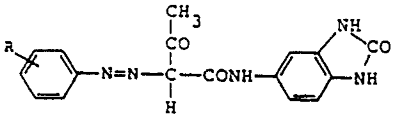


Example of the structures of monoazo pigment
(R.Gacher and H.Muller 1987:488)

Fig. 3



Example of a yellow azo condensation pigment

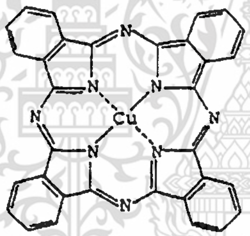


Example of the structures of diazo pigment
(R.Gacher and H.Muller 1987:488)

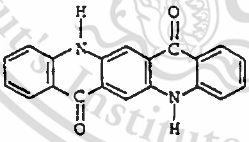
2.2 Non-azo pigments

The example of non-azo pigment is phthalocyanine that is present in several crystalline forms, of which the stabilized α and β forms are especially important. These pigments for the most part contain copper bound in complexes, however, there are also some metal-free types. Phthalocyanines are highly stable to light and heat. The examples of non-azo pigments are shown in Fig. 4

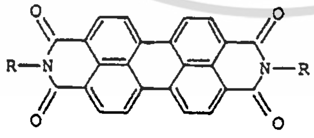
Fig. 4



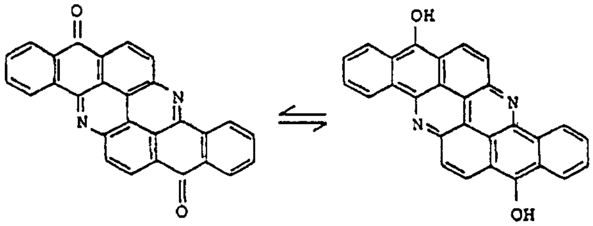
Cu-phthalocyanine (C.I. Pigment Blue 15, 16; C.I. Pigment Green 7, 36; C.I. Solvent Blue 70)



Trans-quinacridone (C.I. Pigment Red 122, 209; C.I. Pigment Violet 19)



Perylene tetracarboxylic acid derivative (C.I. Pigment Red 123, 149, 178)



Flavanthrone (C.I. Pigment Yellow 24)

Example of non-azo pigments
(R.Gacher and H.Muller 1987:492)

Colour

Colour is a sensation that is aroused when light falls on the retina of the eye. Light may be perceived either as originating directly from a light source or as reflected light. White light is perceived as colourless because the eye is completely attuned to the characteristics of such light, and only a neutral colour sensation is aroused by it. Colour perception depends on the different degrees to which various wavelengths of light stimulate the eye.

Characteristics of Colour

Every colour has three basic characteristics. They are (1) hue, (2) lightness, and (3) chroma. Colour experts describe an object's colour in terms of these characteristics.

1. **Hue** is the property that gives a colour its name for example, red, orange, yellow, green, blue, or violet or a combination of such names. The dramatic differences that we see among the colours in the spectrum are produced by very slight differences in the wavelengths of light. For example, the wavelengths that appear as yellow are only slightly shorter than those of orange. But there is a great visual difference between orange and yellow. This difference is a difference in hue.

2. **Lightness** is a measurement of the amount of light reflected from a coloured object. The lightness of a colour may be expressed by comparing the colour's level of reflected light with that of samples on a

lightness scale. A lightness scale runs from black, through shades of gray, to white. Black reflects very little light. A colour that reflects about the same amount of light as black has a very low lightness level. Gray reflects more light than black. Thus, a colour that reflects about the same amount of light as a shade of gray may have an intermediate level of lightness. White reflects nearly all the light that strikes it. Therefore, a colour that reflects about the same amount of light as white has a very high lightness level. Colour experts use the term brightness to describe the lightness level of a coloured light source.

3. **Chroma** is a measurement of the saturation (concentration) of a colour. For example, a teaspoon of red poster paint powder mixed with a teaspoon of water produces paint of a deep red colour. The paint has a high concentration of red colourant, and so it has a high chroma. But when the paint is diluted with a cup of water, the resulting mixture will have a low concentration of red colourant and, therefore, a low chroma.

How Colours Are Classified

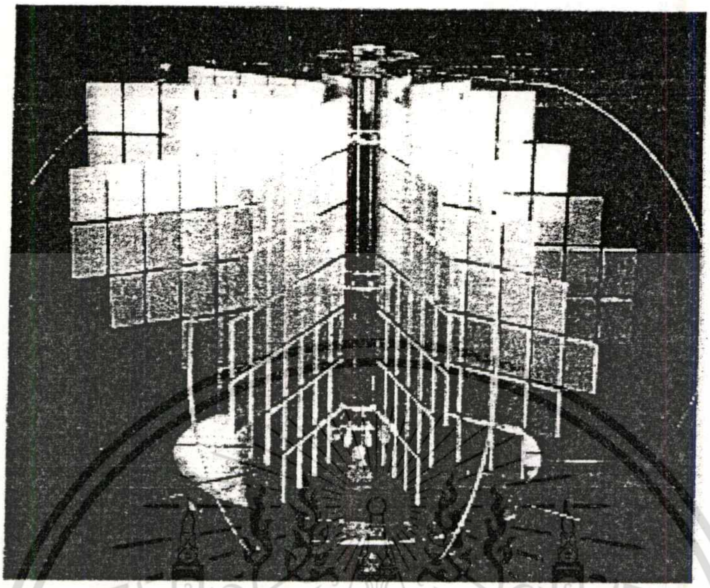
Experts estimate that colours can be distinguished perhaps as many as 10 million colours. Each colour differs from all others in some degree of hue, lightness, or chroma. Names for colours are far too inexact to describe accurately all the colours observed. As a result, people often have difficulty trying to describe or match a certain colour. Matching colours is especially important in such industries as paint and textile manufacturing. Manufacturers of paints and textiles must minimize differences in the colour of a particular paint or fabric from one batch of paint or bolt of fabric to another.

To overcome problems in describing and matching colours, colour experts have developed various systems of classifying colours. Two widely used classification systems are :

1. The Munsell Colour System

The Munsell Colour System is one of the most popular and useful means of classifying colours. It was developed in the early 1900's by Albert H. Munsell, an American portrait painter. The system classifies colours according to the three basic characteristics of **hue**, **lightness**, and **chroma**. However, Munsell used the term **value** for lightness. The Munsell system may be displayed in many ways. A common display shows samples of different colours arranged around a vertical axis. Different hues are arranged around the axis like the spokes of a wheel, with each spoke consisting of a different hue. The axis serves as the value, or lightness, scale. It is divided into 10 sections. These sections correspond to 10 levels of value from black at the bottom, through shades of gray, to white at the top. All colour samples at the same level have the same value. Colours close to the axis have low chroma. The farther from the axis a colour is located, the higher is its chroma. The example of Munsell system is shown in Fig. 5

Fig. 5



Munsell Colour Space

To match a particular colour using the Munsell system or a similar system, one must find that colour among the colour samples provided. However, the number of samples in such systems cannot approach the number of colours we are able to distinguish. For this reason, it is sometimes impossible to find an exact colour match.

2. The CIE System of colour specification

The CIE System of Colour Specification. Manufacturers of such products as foods, paints, paper, plastics, and textiles must often match colours precisely. Because colour vision varies among people, two colours that match for one person may not match for another. For this reason, manufacturers do not rely on the human eye to match colours precisely. Instead, they use the CIE System of Colour Specification. CIE stands for "Commission Internationale de l'Eclairage" (International

Commission on Illumination), an international organization that establishes standards for measuring colour.

The red, green and blue primaries of the CIE system are described by spectral response curves which were derived from the average results of colour matching experiments made by a number of observers having normal colour vision. The response curves most commonly used refer to a matching field subtending an angle of 2° at the eye; this defines the 1931 CIE standard observer. More recently, data for a 10° visual field have become available (1964 CIE 10° standard observer).

The CIE standard observer response curves $\overline{X}$(red), $\overline{Y}$(green), $\overline{Z}$(blue) give the amounts $\overline{X}_\lambda$, $\overline{Y}_\lambda$, $\overline{Z}_\lambda$ of the red, green and blue primaries respectively, required by the Standard Observer to match light of wavelength lamda. In addition, Y is arranged to correspond exactly to the average luminous curve for an average eye. Thus the CIE description of a colour can be derived from its reflectance spectrum by multiplying the percentage reflectance at each wavelength R by the appropriate values of $\overline{X}_\lambda$, $\overline{Y}_\lambda$, $\overline{Z}_\lambda$. It is also necessary to take into account the energy distribution of the light in which the colour is to be viewed, viz E. The CIE tritimulus values are then :

$$X = \sum_{400}^{700} E_l . R_l \overline{X}_l \qquad (1)$$

$$Y = \sum_{400}^{700} E_l . R_l \overline{Y}_l \qquad (2)$$

$$Z = \sum_{400}^{700} E_l . R_l \overline{Z}_l \qquad (3)$$

Y is also a direct measure of luminosity (luminous reflectance). For a perfect black Y=0 and for a perfect white Y=100. Photoelectric colourimeters are available that give X, Y and Z directly.

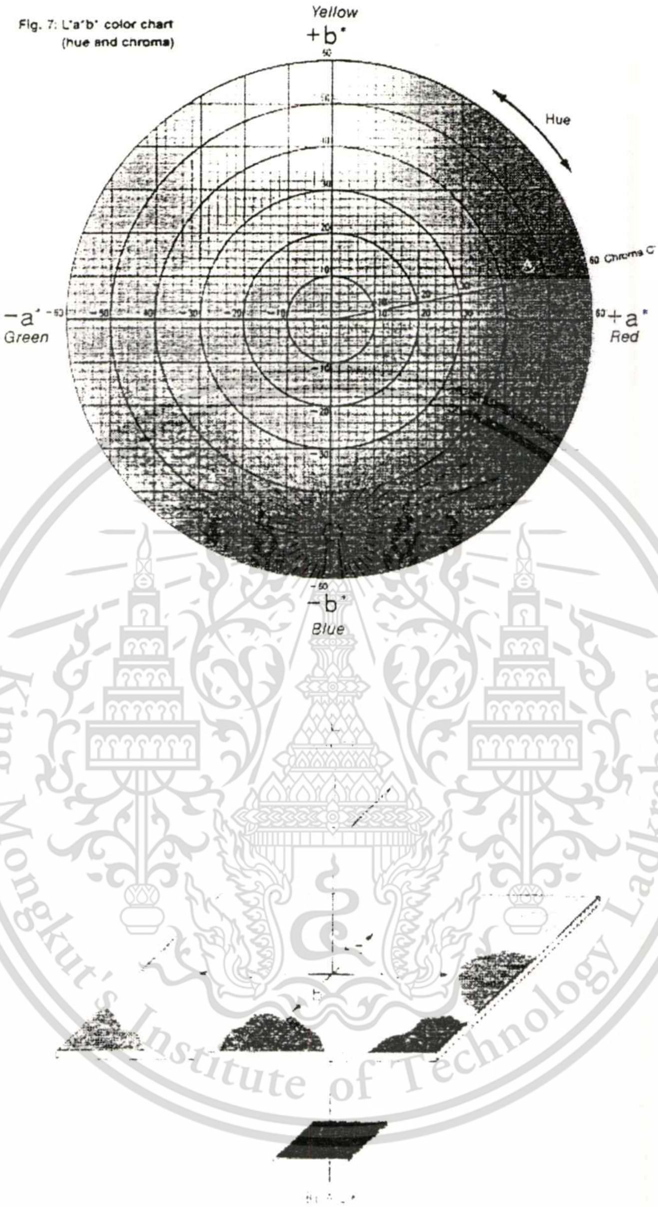
Graphical presentation of tristimulus values would require a three-dimensional coordinate system, and so three new quantities, the chromaticity coordinates, are derived from X, Y and Z as follows :

$$x = \frac{Y}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Y}{X+Y+Z} \qquad (4)$$

Since x+y+z=1, x and y alone are sufficient to describe the colour, disreguarding luminosity.

Adums and Nickerson derived quantitative relations between the Munsell parameters value, hue and chroma and the CIE-tristimuli X, Y and Z. In 1976 the International Commission of Illumination (CIE) recommended the so-called Lab system as universal standard. The letters L*, a* and b* refer to the three axes of the system, a lightness axis (L*) and two axes representing both hue and chroma, namely a red-green axis (a*) and a blue-yellow axis (b*) as shown in Fig. 6. The CIE L*a*b* system has the advantage that colour differences dE (which d is delta and E is German word "Empfindung" means felling) can be determined with the aid of relatively simple computer programs.

Fig. 6



CIE Colour System

Colour difference equation

CIELab Colour Differences

By using the coordinate systems to describe colour, we can also describe changes in colour. With proper instrumentation, even minute changes in colour can be measured. For example, in the CIE L*a*b* system, the difference in colour denoted DE, can be found between two samples.

$$\Delta E_{CIEL^*a^*b^*} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (5)$$

where L* = lightness/darkness

a* = red/green

b* = yellow/blue

CMC Colour Difference

The above colour difference calculations determine a spherical acceptance tolerance. Unfortunately, most experimentally determined colour acceptance limits are not spherical but rather elliptical or even asymmetric. The longest axis of the ellipse is usually in the lightness/darkness direction, followed by the "Chroma" direction (pointing away from gray), especially in intense colours. For example, when look at a Red Delicious Apple, it is assumed that the more intense the red, the better tasting the apple will be. However, if ones were to perform a colour control function on Red Delicious Apples, ones would have a higher tolerance for "depth of red" appearance than other would for yellowness. The final colour acceptance shape might have an acceptable Da* (red/green) of 2 but only an acceptable Db* (yellow/blue) of 0.5.

In order to mathematically model this favoritism, there is another colour difference calculation referred to as CMC colour differences. (named after the Colour Measurement Committee of the Society of Dyers and Colourists) It can be quite complex and is limited in use in by several material suppliers for adaptation in the automotive field.

CMC DE is calculated by applying an elliptical formula to the CIE L*a*b* values and applying different axes favoritism based on where the particular colour lies in the colour space. There is also an experimentally determined lightness to chroma (l:c) ratio for each material in question. Typically, soft goods (fabrics) would use a lower value than hard goods (paint, plastic.) As in order colour difference equations, one must also experimentally determine the acceptable DE_{cmc} for each colour. (refered to as the commercial factor, compare in this system.)

Below is the formula with all of the supporting calculations included. There are also example values and calculations for a Red Delicious apple and a light gray to compare the DE(L*a*b*) and the DE(CMC) calculations.

First convert the a* and b* (rectangular coordinates data) to the C* and h polar coordinates for chroma (distance from 0 colour or neutral gray) and hue (Angle in degree, where red =0) as shown and then apply remaining calculations.

$$C^* = \sqrt{(a^*)^2 + (b^*)^2}$$

$$h = \arctan({}^{b^*}\!/_{a^*})$$

$$S_L = \frac{0.040975L^*}{1 + 0.01765L^*}$$

$$S_L = 0.511$$

$$F = \sqrt{\frac{C^{*4}}{C^{*4} + 1900}}$$

T=0.36+abs[0.4cos(35+h)] for h<164 and h>345

T=0.56+abs[0.2cos(168+h)] for 164<h<345

$$S_C = \frac{0.0638C^*}{1 + 0.0131C^*} + 0.638$$

$$S_h = (FT + 1 - F)S_C$$

$$\Delta E_{CMC} = \sqrt{\left(\frac{\Delta L^*}{l:c}\right)^2 + \left(\frac{\Delta C^*}{S_c}\right)^2 + \left(\frac{\Delta h}{S_h}\right)^2} \qquad (6)$$

Instruments to Measure Colour

There are two main types of instrumentation used to measure the colour of an object; **colourimeter** and **spectrophotometer**. Since there are many factors that will affect the perceived colour of an object, it is important to understand that instrumental values should be used in conjunction with visual assessments to provide the best possible information on the colour of an object. All instruments should be calibrated and proven valid before using for colour approvals.

Colourimeter

With colourimeters, colour measurements are made with a photoelectric instrument using 3 or 4 coloured lights, which illuminate

Processing of Natural Rubber

The manufacture of rubber products from dry NR can be divided into four stages: mastication, mixing and compounding, shaping and vulcanisation.

1. Mastication

Mastication can be briefly described as the operation of softening and viscosity reduction of raw rubber, either mechanically or by mechano-chemical degradation. At the early stage of mastication , the reduction in rubber viscosity is primarily due to chain extension under the action of the applied stress leading to chain scission due to the continuing shear. Moreover, the presence of oxygen at elevated temperature leads to an oxidative chain scission reaction.

2. Mixing and Compounding

Mixing is the process whereby the particulates of bulk fillers and minor components are dispersed into the polymer matrix to give a uniform and homogeneously mixed compound.

The colourants will be applied during this stages. The dispersion of colourants can be subdivided into the following steps :

2.1 breakdown

2.2 wetting

2.3 distribution

2.4 stabilization

3. Vulcanisation of Natural Rubber

Vulcanisation is an irreversible process during which a rubber compound ,through a change in its chemical structure into a network by crosslinking. Sulphur vulcanisation is still the most widely used method of crosslinking natural rubber. In natural rubber compounds, except ebonite, the amount of sulphur (S) used can be varied from 3.5 phr down to only 0.4 phr. The accelerated sulphur vulcanisation systems can be classified into three types :

3.1 Conventional systems containing high sulphur/accelerator ratios

3.2. Efficient (EV) systems containing high accelarator/sulphur ratios

3.3. Semi-EV systems that are intermediate between conventional and efficient systems.

Table 1
Vulcanisation Systems for Natural Rubber
(C.M.Blow and C.Hepburn 1985: 196)

Systems	Sulphur (S) phr	Accelerator (A) phr	A/S
Conventional (CV)	2.0-3.5	1.2-0.4	0.1-0.6
Semi-EV	1.0-1.7	2.5-1.2	0.7-2.5
EV	0.4-0.8	5.0-2.0	2.5-1.2

There are mono-, di or polysulphidic depending on the molar ratio of accelerator to sulphur used (or vulcanisation systems). They also depend on the concentration of activators, and on the time and temperature of vulcanisation.

Table 2
Vulcanisate Structures and Properties
(C.M.Blow and C.Hepburn 1985: 196)

Properties	CV	Semi-EV	EV
Poly- and disulphidic crosslink, %	95	50	20
Monosulphidic crosslink, %	5	50	80
Cyclic sulphidic concentration	High	Medium	Low
Low-temperature crystallisation resistance	High	Medium	Low
Heat-aging resistance	Low	Medium	High
Reversion resistance	Low	Medium	High
Compression set, 22 hr at 70 C, %	30	20	10

Conventional systems give vulcanisates which possess excellent initial properties like strength, resilience and resistance to fatique and abration, and are satisfactory for many applications. However, their heat-aging resistance, creep and stress-relaxation properties are less satisfactory. For good heat-aging resistance and low compression set, an EV system is essential, or a semi-EV system may be chosen as a compromise between cost/performance. EV systems can also be vulcanized at higher temperatures (180-200 °C) and are less antagonistic to antioxidants than conventional systems.

Discolouration of Rubber Compounds

The following are guidelines for the development of good base compound for the production of coloured rubber product.

1. Use clean, light coloured rubber.

2. Dark coloured fillers and softeners should be avoided especially where bright, light colours are desired.

3. Light coloured plasticizers and resins should be selected, preferably of the non-reactive type.

4. Antioxidants should be of the non-staining and non-discolouring type. Phenolic antioxidants are recommended.

5. Thiazole and thiuram accelerators are recommended. Some sulfenamide and dithiocarbamate types can also be used.

6. No copper bearing materials can be used, nor should products that provide an alkaline reaction, such as ureas, aldehydeamines and diphynyl guinidine, because they may discolour the compound or consume the colour.

7. Mixing and processing

Both processing and curing temperatures can be critical to coloured compounds that use organic colour pigments. Temperatures above 163 °C are not recommended.

Cured products, especially mats or other flat products, must be cooled sufficiently before stacking to avoid a heat degradation in the center of the stack that may result in colour change.

Chapter 3

Experimental

Materials

Compound Formulations

The rubber compounds selected for the investigation are list in table 3.

Table 3
Formulation of rubber compounds used in this study

Formula	Shoe Sole	Rubber Band
Natural Rubber	100	100
Zinc oxide	5	1
Sulphur	1.2	2
Stearic acid	3	1
PVI	0.6	0.6
CBS	2	-
TMTD	0.3	-
MBTS	-	1
TMTM	-	0.1
22CP46	1	1

Specification for materials

Table 4
Specification for materials

Materials	Specification
Natural Rubber	TTR 5L
Zinc oxide	Active
Sulphur	Commercial
Stearic acid	Commercial
Antioxidant	22CP46
PVI	Commercial
CBS	Commercial
TMTD	Commercial
TMTM	Commercial
MBTS	Commercial

Colour Masterbatch

There are eight colour masterbatches which were used for this study. The colour masterbatches are organic pigments mixed with styrene butyl rubber (SBR). These colour masterbatches were reported that it faded in colour when prepared the final products. The concentration of organic pigments are shown in Table 5.

Table 5
Masterbatch concentration

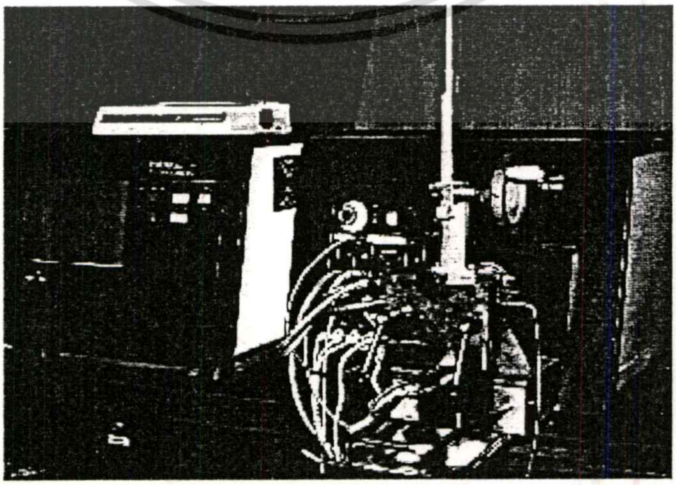
Colour	Abbreviation	Concentration (w/w on SBR)
Red/Orange	R/O	60
Red	R	50
Violet/Pink	V/P	50
Purple	P	20
Green-A	GA	50
Green-B	GB	60
Blue-A	BA	50
Blue-B	BB	60

Compounding

Equipment

Mixing was carried out on a "Haake Rheocord 90" computer controlled miniature internal mixer as shown in Fig.7. The mixer has a chamber volume of 77 cm^3 and contains intermeshing rotors.

Fig. 7



Haake Rheocord 90 computer controlled miniature internal mixer

Mixing Conditions

The mixing conditions e.g. rotor speed, fill factor were fixed. The chamber temperature were controlled at 40,90,120 and 150 °C. The mixing condition are shown in table 6.

Table 6
Mixing conditions

Variables	Conditions
Fill factor	0.7
Rotor speed (rpm)	60
Chamber temperature (°C)	40,90,120,150

Mixing Procedure

A mixing procedure was carried out base on ASTM D3182. The rubber was masticated for 3 minutes and then all ingredients were fed to the mixer. The mixing period was 5 minutes. After that the mixed was discharged manually to a two roll mill in order to dissipate the heat and sheet out the compound. (For mixing temperature 150°C, the overall mixing time was 3 minutes to prevent scorch in mixing chamber.)

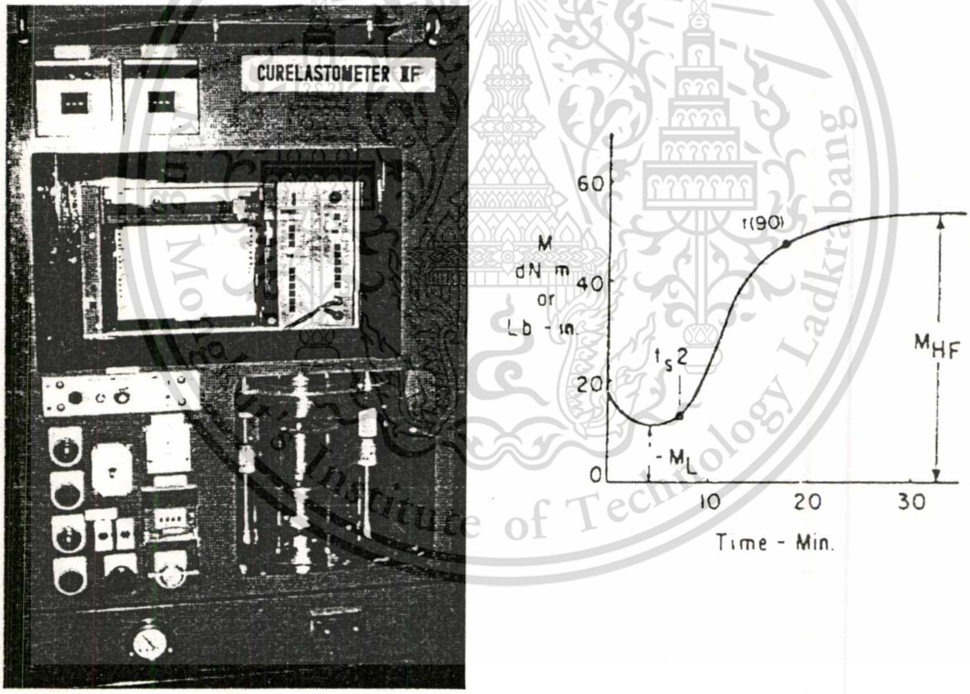
Preparation of Vulcanised Sheets

Determination of Cure Curve

1. Equipment

Shimadzu Curelastometer (Model : Curelastometer IIF) was used for determining the vulcanisation characteristics for each rubber compounds. The instrument is shown in Fig.8a.

Fig. 8



a. Curelastometer

b. Cure curve

2. Procedure (Based on ASTM D 2084)

For all tests on Curelastometer, about 3 grams of sample are required and the testing conditions are given in table 7.

Table 7
Testing Conditions for the Measurement of Cure Curve

Parameters	Condition
Temperature (°C)	120,140,150
Frequency (Hz)	1.7

3. Analysis of the Cure Curve

The measurement of vulcanisation characteristics, cure time t_x , can be calculated from the curve of torque versus time (Fig.8 b.).

t_x is equal to the time to x % of maximum torque or t_x = minutes to $M_L + x(M_H-M_L)/100$

M_L= Minimum torque (N.m)

M_H= Maximum torque (N.m)

The t_{70}, t_{90} and t_{110} were calculated for each sample.

Vulcanisation of Samples

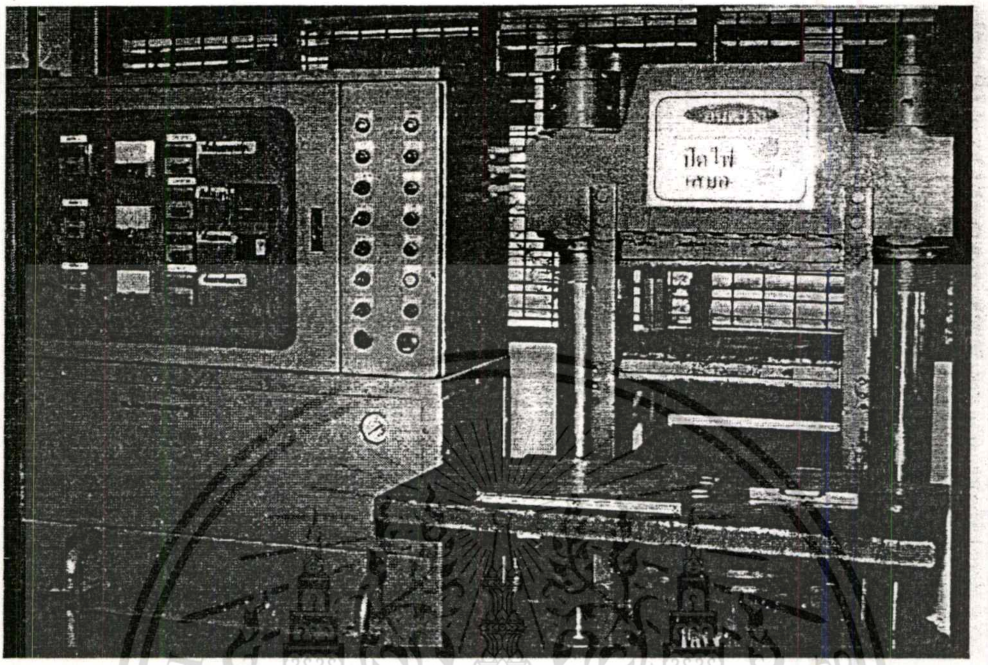
1. Equipment

The hot press and moulds were used to prepare flat moulded sheet at pressure of 1000 psi and controlled at constant cure temperature. The hot press and moulds are shown in Figs. 9 and 10 respectively.

2. Vulcanization Procedure

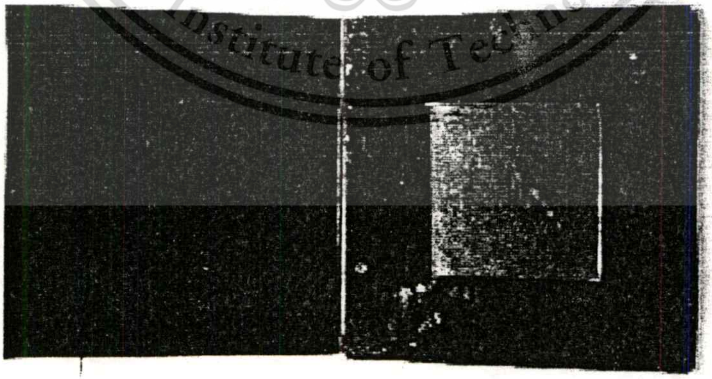
The test samples were moulded into 1.25 mm in thickness at four different cure conditions. The curing conditions are given in Table 8.

Fig. 9



Hot press

Fig. 10



Stainless steel Moulds

Table 8
Curing Conditions

Rubber Band	Masterbatch (phr)	TEMP (°C)	t_x x
	0.1,0.5	120	90
(Standard)		140	90
		150	90
		140	70
		140	110
Shoe sole	Masterbatch (phr)	TEMP (°C)	t_x x
	0.1,0.5	120	90
		140	90
(Standard)		150	90
		150	70
		150	110

Colour Difference Measurement

Equipment

The equipment employed for this measurement was a ICS-TEXICON instrumental colour systems. The system comprises a spectrophotometer, computer and printer.

Procedure

Set the parameters for ICS-TEXICON as follows:

Colour Difference Equations : CIELAB

Illuminants : D65-10’

The standard sample was placed on the sample holder to measure a reference value. Then batch samples were measured the colour difference compared to the reference value called DE Value. The samples of printout report are shown in appendix 1.

Colour Dispersion Measurement

Apparatus

Scanning Electron Microscope (SEM) : HITACHI

Model : S-2500

Test Specimen

Samples were cut in cross-section from flat sheet of vulcanised rubber and coated with platinum and lead. The magnification used are 2000 times and operating voltage is 15 KV.

Hardness Measurement

The type A durometer is used for measuring the sample. The test method is based on ASTM D 2240 “Standard Test Method for Rubber Property -Durometer Hardness”.

Apparatus

Model : ats faar, Italia

Type : Shore A

Test Specimen

The samples are 1.25 mm in thickness and they were composed of 4 plied pieces to obtain the specimen of 5 mm thickness.

Hardness Report

Material Tested : Vulcanised NR

Test Specimen : 5 mm thickness

4 plied pieces

Test Temperature: 27 °C

Durometer Type : Shore A

FT-IR Measurement

Apparatus

Fourier Transform Infrared Spectrophotometer (FTIR)

Model : Perkin-Elmer 2000

Test Specimen

Samples were placed on KRS-5 reflectance.

FT-Raman Measurement

Apparatus

Fourier Transform Infrared Spectrophotometer with Raman

Model : Perkin-Elmer System 2000 NIR FT-Raman

Test Specimen : Flatted plain specimen

Chapter 4

Results and Data Analysis

Curing Conditions Data

The curing time for each conditions was calculated from cure curve at particular cure level. The results are shown in table 9 for both formulations of rubber band and shoe sole.

Table 9
Curing Time for various conditions

Rubber Band	TEMP (°C)	t_x x	Time at corresponding t_x (min)
(Standard)	120	90	45.0
	140	90	15.0
	150	90	5.8
	140	70	12.4
	140	110	17.6
Shoe sole	TEMP (°C)	t_x x	Time at corresponding t_x (min)
(Standard)	120	90	57.0
	140	90	15.7
	150	90	8.0
	150	70	7.7
	150	110	10.4

The curing temperature which is generally used for vulcanisation of rubber band and shoe sole are 140° and 150° C respectively. To study effect of cure temperature, for rubber band formulation others two temperatures selected for vulcanisation are 120° and 150 ° C. The shoe sole formulation were also vulcanised at 120° and 140 ° C, in order to study the effect of cure temperature and cure time.

Effects of over cure and under cure were carried out by curing at different cure levels (t_{70} and t_{110}). The study was investigated at two different tempeartures i.e. at 140 ° C and 150 ° C.

The curing time shown in Table 9 were used for vulcanisation of all samples which contained 0.1 and 0.5 phr of colour masterbatch concentration.

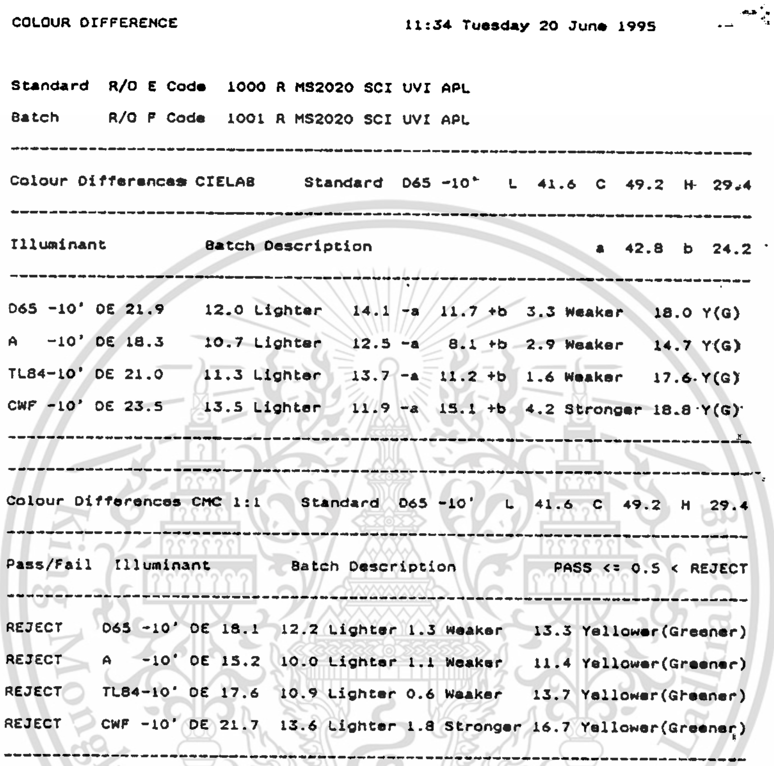
Colour Difference Data

The samples which were prepared with different conditions were then measured colour difference by ICS-TEXICON colour system compared between standard and batch sample. The colour difference values can be obtained from the computer software which provided equations for CIEL*a*b* and CMC(1:1).

Fig. 11 shows the print out of colour difference values for red/orange rubber band sample. Standard sample (code 1000 R) was a vulcanised sheet at mixed temperature of 40° C and batch sample (code 1001 R) was a vulcanised sheet mixed at 90° C. The first section shows the CIEL*a*b* equation with daylight illuminant and 10 ° observation

(D65-10') and the value of munsell system Lightness (L*) 41.6, Chroma (C) 49.2 and Hue (H) 29.4.

Fig. 11



```
COLOUR DIFFERENCE                    11:34 Tuesday 20 June 1995

Standard  R/O E Code  1000 R MS2020 SCI UVI APL
Batch     R/O F Code  1001 R MS2020 SCI UVI APL
---------------------------------------------------------------------------
Colour Differences CIELAB     Standard  D65 -10'   L  41.6  C  49.2  H  29.4
---------------------------------------------------------------------------
Illuminant          Batch Description                        a  42.8  b  24.2
---------------------------------------------------------------------------
D65 -10' DE 21.9    12.0 Lighter   14.1 -a  11.7 +b  3.3 Weaker   18.0 Y(G)
A   -10' DE 18.3    10.7 Lighter   12.5 -a   8.1 +b  2.9 Weaker   14.7 Y(G)
TL84-10' DE 21.0    11.3 Lighter   13.7 -a  11.2 +b  1.6 Weaker   17.6 Y(G)
CWF -10' DE 23.5    13.5 Lighter   11.9 -a  15.1 +b  4.2 Stronger 18.8 Y(G)
---------------------------------------------------------------------------

---------------------------------------------------------------------------
Colour Differences CMC 1:1    Standard  D65 -10'   L  41.6  C  49.2  H  29.4
---------------------------------------------------------------------------
Pass/Fail  Illuminant        Batch Description          PASS <= 0.5 < REJECT
---------------------------------------------------------------------------
REJECT     D65 -10' DE 18.1  12.2 Lighter 1.3 Weaker   13.3 Yellower(Greener)
REJECT     A   -10' DE 15.2  10.0 Lighter 1.1 Weaker   11.4 Yellower(Greener)
REJECT     TL84-10' DE 17.6  10.9 Lighter 0.6 Weaker   13.7 Yellower(Greener)
REJECT     CWF -10' DE 21.7  13.6 Lighter 1.8 Stronger 16.7 Yellower(Greener)
---------------------------------------------------------------------------
```

Print out report of ICS-Texicon colour system

The next row shows the value of green-red axis (a*) 42.8 and yellow-blue axis (b*) 24.2 of the standard sample. There are four light sources used for each calculation i.e. :-

D65	Daylight
A	Tungsten
TL84	Mark&Spencer store
CWF	Cool White Fluorescent

Light sources can also affect the perceived colour of samples. Therefore, it is important to specify a light source when viewing and matching colour. The D65 is a light source which can be used to represent natural daylight. It is preferred for matching colour and colour difference calculation. The other light sources are also shown in print out results which the measurement values are close to D65 results. Thus, this study uses only D65 results for discussion of colour difference.

The first column shows the DE (colour difference) value which can be calculated from equation 15. It is needed to bear in mind that the accepted DE value should not be more than 0.5. The example of print out was 21.9 shown that the standard and batch did not match.

The second column is DL* (difference in lightness) 12.0 lighter than standard. The next column was a green-red axis and yellow-blue axis ,the 14.1 -a* mean the batch shift to green side by 14.1 units and 11.7 +b* mean the batch shift to yellow side by 11.7 units. (see Fig. 6)

The last two columns are DC (difference in chroma) and DH (difference in hue). The value of 3.3 weaker mean its chroma of batch was weaker than standard 3.3 units and 18.0 Y(G) mean its hue of batch was shifted to yellow/green side by 18.0 units.

The other colour differences shown in next section of print out results are CMC(1:1) equation which is also used in industrial processing for approval of product. The pass or reject depended on the DE value as well as the values obtained from CIEL*a*b* equation.

Likewise, other columns also show DL*, DC and DH comparing between those of standard and batch.

Effect of Process Variables

The Mixing Temperature and Masterbatch Concentration

The first colour masterbatch which was used for this investigation of the mixing temperature and masterbatch concentration was red/orange. This colour was reported from the supplier that the colour match was rejected when final products were measured.

Table 10

Colour difference measurement of 0.1 phr red/orange rubber band

COLOUR DIFFERENCE CIELAB D65-10'

TEMP(°C)		L*	a*	b*	C	H
40(Standard)		41.6	42.8	24.2	49.2	24.2
TEMP(°C)	DE	DL*	a*	b*	DC	DH
90	21.9	12.0	-14.1	11.7	3.3	18.0YG
120	25.2	14.0	-17.1	12.3	4.5	20.5YG
150	30.9	16.0	-23.3	12.6	7.6	25.4YG

It can be seen from Table 10 that when mixing temperature increase from 40° C to 90° C the DE was 21.9. This DE or ΔE can be calculated by equation 15.

$$\Delta E_{CIEL^*a^*b^*} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

$$= \sqrt{(12.0)^2 + (-14.1)^2 + (11.7)^2}$$

$$= 21.9$$

Another value that affected the appearance of sample was a DH. It is shown that when mixing temperature increase from 90° to 120° and 150°C DH of Red/Orange shift to yellow/green side by 18, 20.5 and 25.4 units respectively.

Table 11
Colour difference measurement of 0.5 phr red/orange rubber band

COLOUR DIFFERENCE CIELAB D65-10'

TEMP(°C)		L*	a*	b*	C	H
40(Standard)		37.4	36.2	14.9	39.1	22.4
TEMP(°C)	DE	DL*	a*	b*	DC	DH
90	7.6	4.6	1.8	5.8	4.1	4.5YG
120	8.5	7.8	-0.6	3.4	0.9	3.3YG
150	20.2	13.0	-6.1	14.2	2.8	15.3YG

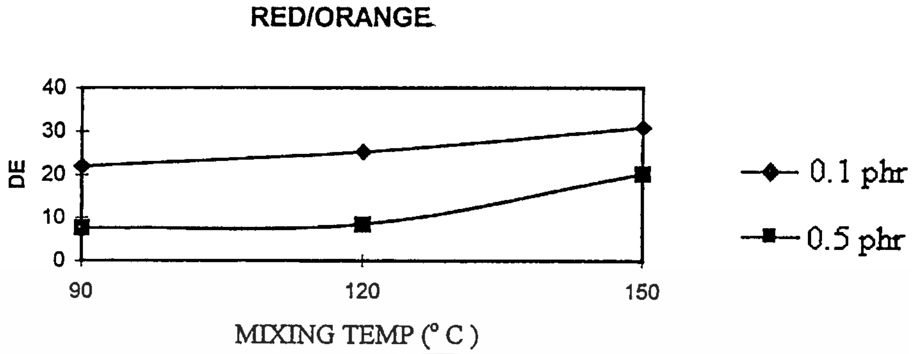
Table 11 shows colour measurement of rubber band sample with 0.5 phr of red/orange colour masterbatch. When compared to 0.1 phr of same colour it was found that the DE value of 0.5 phr was smaller than that of 0.1 phr. Also the DH are shift to yellow/green axis only 4.5, 3.3 and 15.3 units in corresponding to mixed temperature of 90°, 120° and 150°C respectively.

From tables 10 and 11, the plots of DE value against mixing temperature can be developed and shown in Fig.12.

The symbolic used in the graph are shown as follows:-

—◆— Rubber band with 0.1 phr colour masterbatch
—■— Rubber band with 0.5 phr colour masterbatch
—▲— Shoe sole with 0.1 phr colour masterbatch
—×— Shoe sole with 0.5 phr colour masterbatch

Fig.12

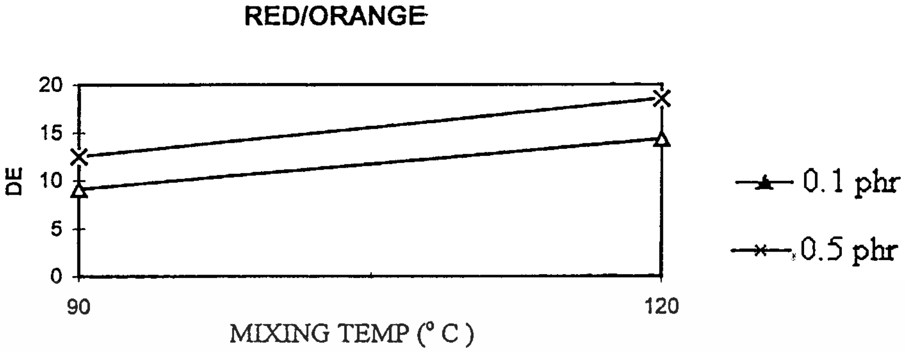


Effect of Mixing Temperature on Red/Orange Rubber band

It can be seen from Fig. 12 that the effect of mixing temperature on red/orange colour masterbatch of rubber band with 0.1 and 0.5 phr of masterbatch concentration show an increase of DE value with increasing temperature. It can be observed that by comparing to its standard, the samples of 0.1 phr colour masterbatch show DE value greater than of 0.5 phr at the same mixing temperature.

Similarly, the plotted of DE value against mixing temperature of shoe sole formulation can be developed from a set of data in appendix A. However, mixing temperature which was used for mixing is 120° C because the rubber shoe sole formulation contains fast curing system. Thus, it is scorchy as the temperature was raised beyond 120° C.

Fig.13



Effect of Mixing Temperature on Red/Orange Shoe sole

Fig.13 illustrates an increase of DE value of rubber shoe sole formulation samples due to an increase of temperature. It can be seen that there is a small change of DE value for both concentration when mixing temperature is increased.

From the above results, it implies that the mixing temperature is a major effect of colour fading. It was reported that the cause of colour fading comes from the dispersion of colour pigments (R.Gacher and H.Muller 1987:512). If inadequate dispersion of pigment, it can manifest itself in the following ways :

- fluctuations in colour intensity,
- deviations in shade,
- streaking.

To investigate the dispersion of pigments, the Scanning Electron Microscope (SEM) photograph was taken as shown in Figs.14 a, b, c and d.

Fig.14

a. b.

c. d.

Scanning Electron Microscope (SEM) photograph of
red/orange rubber band with various mixing temperature
a. 40° C b. 90° C c. 120° C d. 150° C

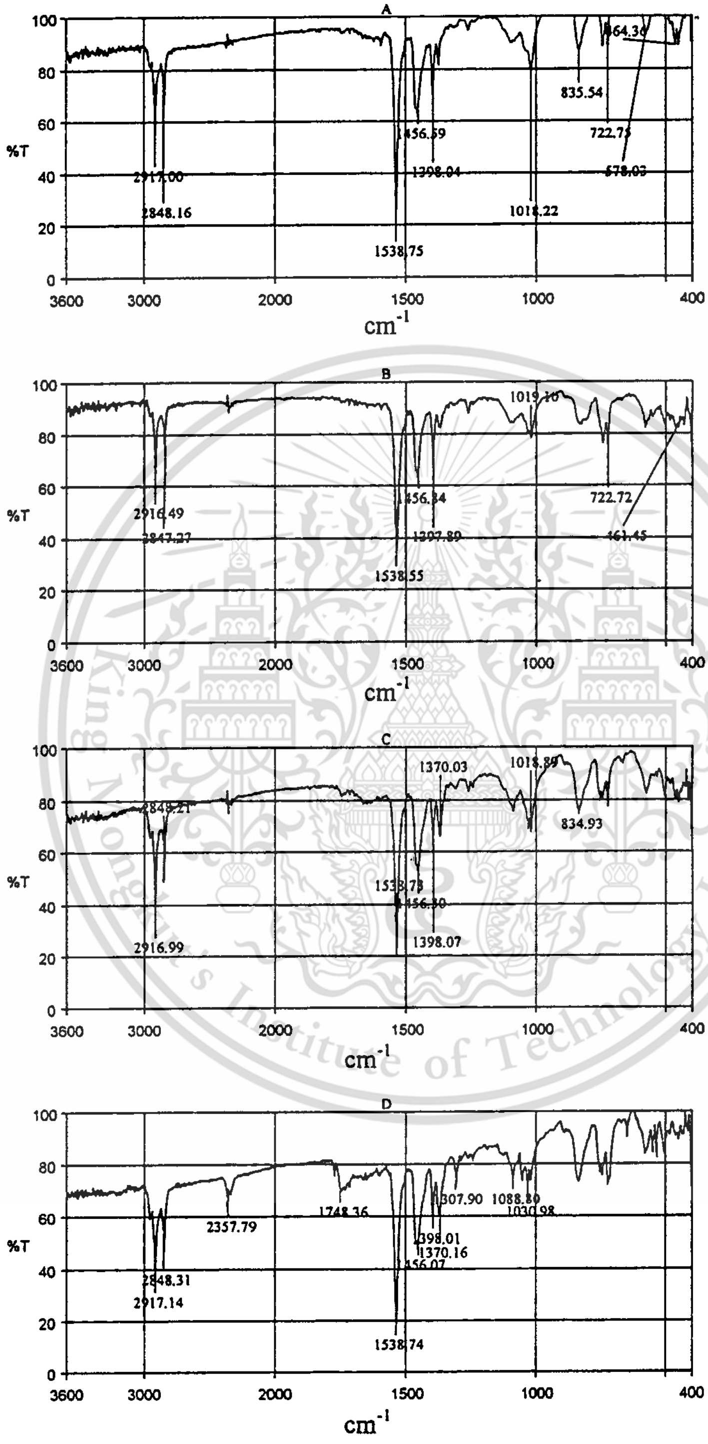
At mixing temperature of 40° C (Fig.14 (a)) , a good dispersion of pigment can be obtained. Due to low mixing temperature, the pigment was broken down by applying shear force to smaller size than that of without applying shear. With increasing temperature to 90° C (Fig.14 b)

, a long rod shape can be observed. It can be explained that the pigments under high mixing temperature condition experience lower shear force than of the observation in Fig. 14 (a). Thus they become aggregates likewise, Fig. 14 (c) and (d) show aggregates and agglomerates of pigments due to high mixing temperatures at 120° C and 150° C respectively.

Besides effect of pigment dispersion, it is believed that effect of chemical change can be another possibility to affect the compound colour fading (R.Gacher and H.Muller 1987:507). For investigation of chemical interaction, the FTIR measurement was employed. Spectrum of samples which were mixed at various temperatures (40-150° C) were illustrated in Fig.15 (a-d).

The technique used was an attenuated total reflectance (ATR) which are invaluable in the characterization (particularly of surface layers) and identification of polymers. This technique rely on the intimate contact of a sample with the surface of a high refractive index, IR-transparent prism. IR radiation entering the prism at an angle greater than the critical is internally reflected at the prism surfaces, but attenuated by absorptions from the sample cantact layer. (B.J. Hunt and M.I. James, 1993:73)

Fig.15



FTIR Spectrum of red/orange rubber band with various mixing temperatures (A) 40° C (B) 90° C (C)120° C and (D) 150° C

The spectrums in Fig.15 (a - d) show traces of typical rubber band compound with red/orange colour. They show that in many simple compounds the -CH_2 group give rise to two frequencies at about 2857 and 2927 cm^{-1} which are, respectively, to the symmetric and antisymmetric stretches of the two C-H bonds. (D.I.Bower and W.F.Maddams 1989:166).

The peaks at 2357 cm^{-1} and 1748 cm^{-1} were C≡N and C=O respectively which shown medium peak at mixing temperature of 150°C. However, lower intensity of those peaks can be found at mixing temperature lower than 150° C.

The aromatic C-H stretching can be found at 1538 cm^{-1} which may come from the accelerators. The region below 1400 cm^{-1} contains many band that arise from other fundamental stretching, vibrations and from coupling of stretches and deformations of adjacent units; this give rise to complex spectra that cannot normally be fully assigned to individual groups.

Thus, it can be clearly seen that degradation of rubber can occur when mixed at high temperature. Similarly, degradation of NR can be formed nitrile compounds with nitrogen from accelerators. It was also reported in Field Colour handbook of GE Plastics that degradation of resin may occur during processing at high temperature. This is a burning of the material and may result in streaking, yellowing, and/or darkening of the product.

The effect of mixing temperature which caused degradation of NR can be studied by preparing rubber band and shoe sole without colour masterbatch. The samples were prepared under condition similar to samples with colour masterbatch. The samples were measured colour difference and the results are shown in Tables 12 and 13.

Table 12
Colour difference measurement of rubber band without masterbatch

COLOUR DIFFERENCE CIELAB D65-10'

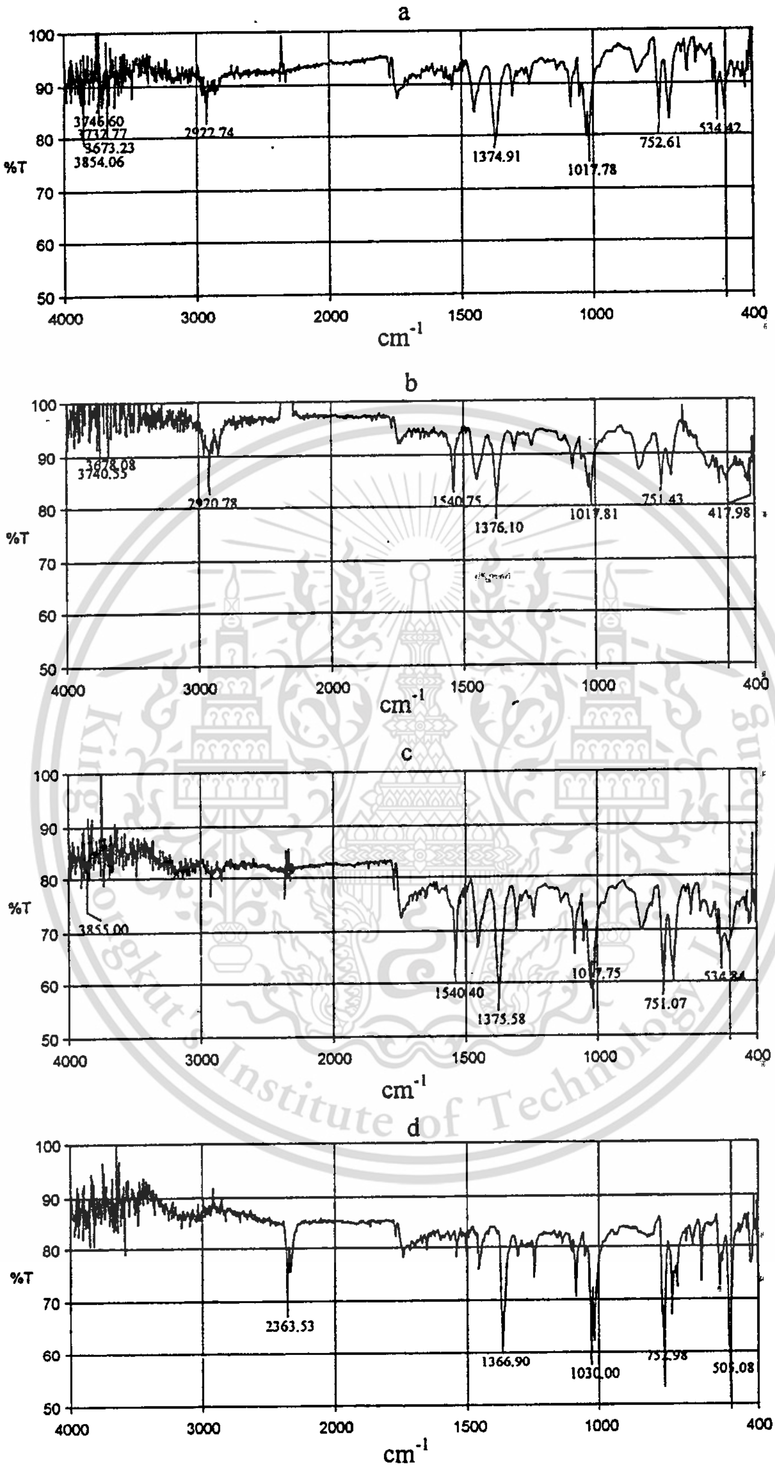
TEMP(°C)		L*	a*	b*	C	H
40(Standard)		65.2	10.4	37.5	38.9	74.5
	DE	DL*	a*	b*	DC	DH
90	4.6	2.4	-2.0	3.4	2.8	2.8YG
120	5.0	0.9	-0.2	4.9	4.7	1.4YG
150	7.4	0.9	-0.9	7.2	6.8	2.6YG

Table 12 shows colour difference of rubber band formulation without colour masterbatch. The DE value changed by 4.6, 5.0 and 7.4 units when mixing temperature raised to 90°, 120° and 150°C respectively. The hue of batch samples were changed to yellow/green side by 2.8, 1.4 and 2.6 units. These mean that the batch samples become yellowish when temperature was raised.

To investigate the yellow colour which may come from degradation of NR, the FT-IR measurement were employed. The spectrum are shown in Fig.16

It can be seen that the carbonyl and nitrile peak which caused from degradation of NR as similar to those of samples with red/orange colour. Thus, it is believed that the high mixing temperature can result in yellowing and darkening in products.

Fig.16



FTIR spectrum of rubber band without colour masterbatch with various mixing temperatures (a) 40° C (b) 90° C (c) 120° C (d) 150° C

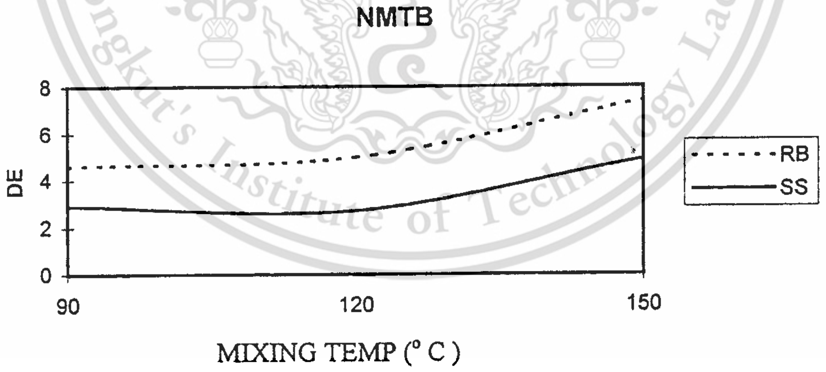
Table 13
Colour difference measurement of shoe sole without masterbatch

COLOUR DIFFERENCE CIELAB D65-10'

TEMP(°C)		L*	a*	b*	C	H
40(Standard)		57.9	13.8	28.1	31.3	63.9
	DE	DL*	a*	b*	DC	DH
90	2.9	2.9	-0.5	0.2		0.5YG
120	2.7	1.3	-0.4	-2.4	-2.3	0.7RB
150	4.9	-0.1	-1.2	-4.7	4.7	1.1RB

Similarly, Table 13 shows the colour difference of shoe sole without colour masterbatch. The colour was also changed due to the raise of mixing temperature.

Fig.17

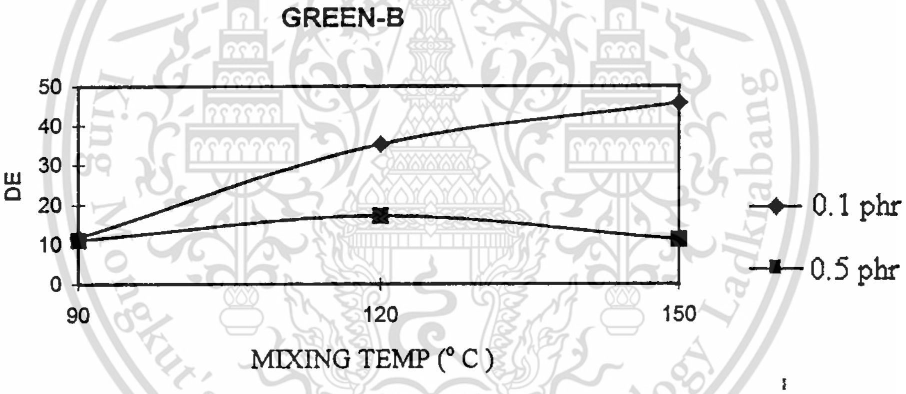


Effect of Mixing Temperature on Rubber band (RB) and Shoe sole (SS) without colour masterbatch

Fig. 17 was obtained by plotting DE against mixing temperature by using data from Tables 12 and 13. It shows the mixing temperature of two vulcanised rubbers with different formulations excluding colour masterbatch. It can be seen that without colour masterbatch the colour of rubber itself changed with mixing temperature. Thus, mixing temperature can cause colour changing. However, the colour different of rubber band is greater than that of shoe sole due to different formulation.

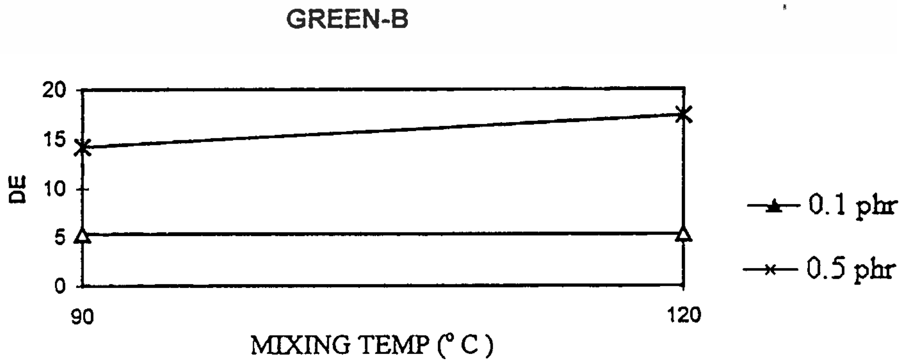
The other colour masterbatch which has a problem with dispersion is Green-B. The colour difference and FTIR spectrum as shown in Figs.18-20.

Fig.18



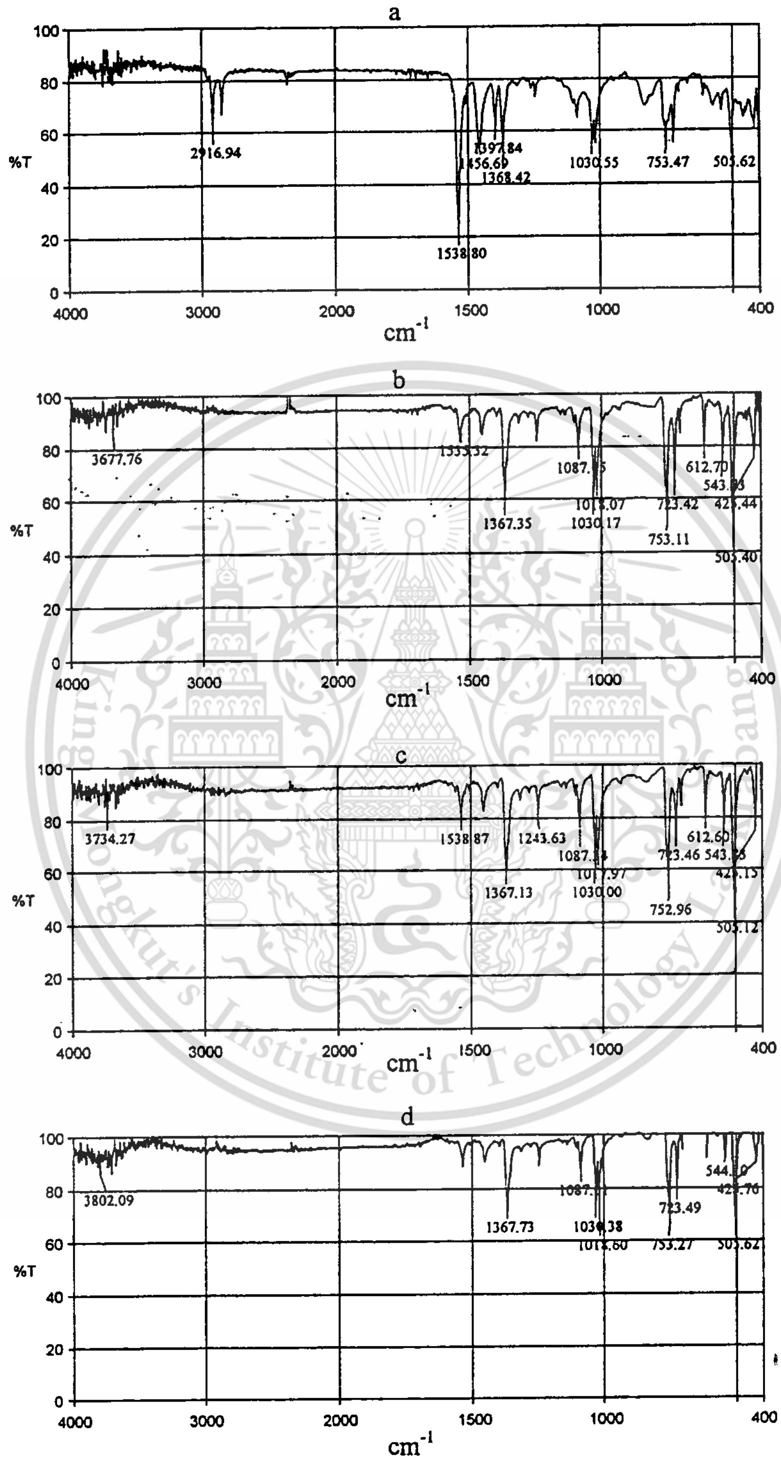
Effect of Mixing Temperature on Green-B Colour Rubber band

Fig.19



Effect of Mixing Temperature on Green-B Colour Shoe sole

Fig.20



FTIR Spectrum of Green-B Rubber band with various mixing temperatures (a) 40° C (b) 90° C (c) 120° C (d) 150° C

It was found from this investigation that Green-B is another colour pigments which is difficult to disperse. It shows a large number of colour difference in both formulations. It can be seen that, particularly, for rubber band formulation (Fig.18) the distinction of DE value, for those 0.1 and 0.5 phr masterbatch, with increasing temperature.

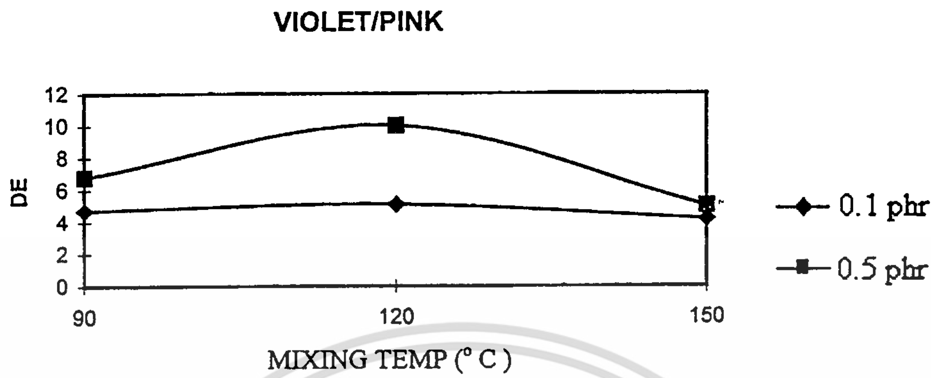
It can be seen from appendix A that the lightness (L*) of 0.1 phr Green-B rubber band shift to white side (positive value) by 5.6, 16.5 and 21.3 units with mixing temperature increase to 90°, 120° and 150°C. That means product becomes lighter green colour. Likewise, the hue ,colour characteristic, shift clockwise to yellow/red side by 6.7, 31.1 and 40.1 units (see Fig. 6).

For 0.5 phr Green-B rubber band the lightness shift to opposite side (negative value) by -7.7, -2.5 and -4.7 units with corresponding to mixing temperature of 90°, 120° and 150° C or product becomes darker green.

Thus, it can be seen that DE of both colour masterbatches, Red/Orange and Green-B, are influenced strongly by the mixing temperature.

The other six colour masterbatches are prepared and studied the colour difference. This groups of colour masterbatches sample represented small DE and cannot be seen any difference in colour by visualisation. Again, the plots of DE value against mixing temperature are shown in Figs. 21-32.

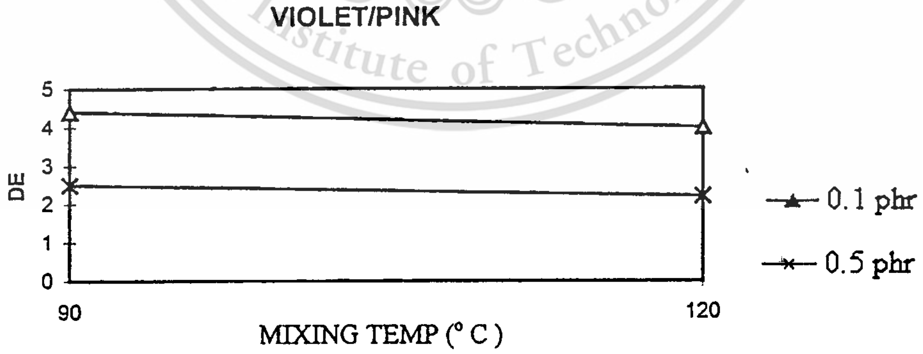
Fig.21



Effect of Mixing Temperature on Violet/Pink Rubber band

Fig. 21 shows DE values with varying mixing temperature of violet/pink colour masterbatch of rubber band formulation. It can be seen that small change in DE value (4-8 units) comparing to first two colour (Red/Orange and Green-B) when mixing temperature increase. However, DE value is still higher than acceptable value.

Fig.22

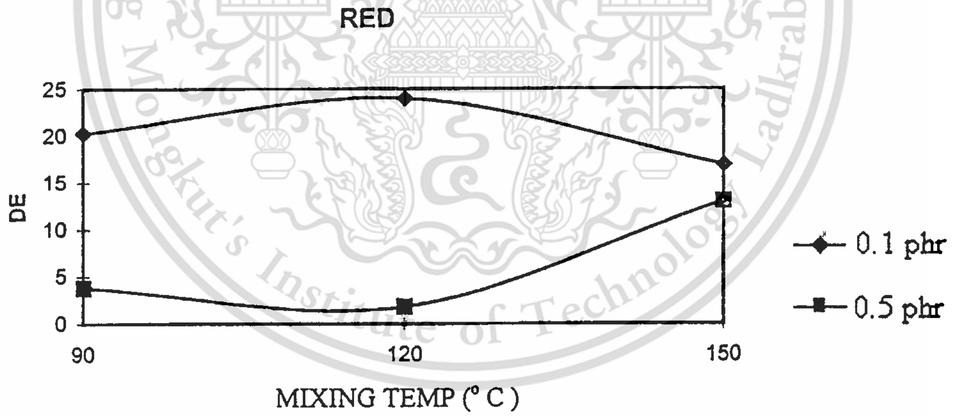


Effect of Mixing Temperature on Violet/Pink Shoe sole

For shoe sole formulation (Fig.22) the DE is almost constant. It was found that the change in DE may be arisen from rubber itself as described in Fig. 17 for rubber formulation without colour masterbatch.

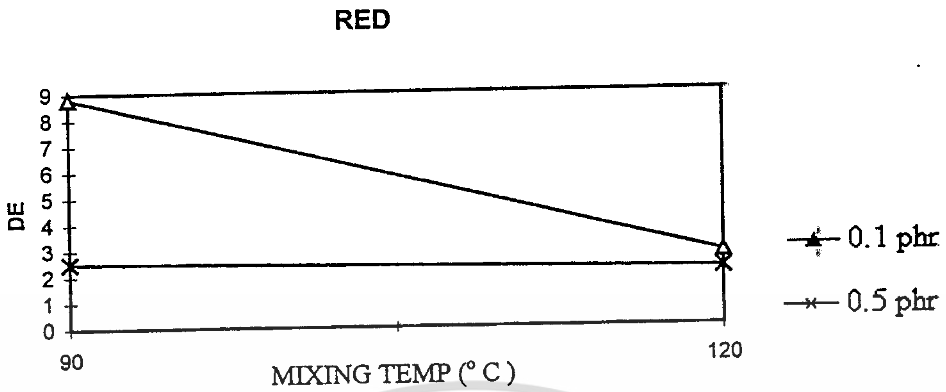
From appendix A, the lightness of 0.1 phr Violet/Pink rubber band shift to lighter side by 3.2, 5.1 and 1.1 units. The hue also shift to yellow/green side by 2.2, 0.6 and 2.7 units. It can be seen that lightness and hue of Violet/Pink shift not so much as the Red/Orange and Green-B do. Similarly, for shoe sole formulae the lightness and hue shift only 1-3 units. This means the Violet/Pink product becomes lighter colour when increase temperature.

Fig.23



Effect of Mixing Temperature on Red Rubber band

Fig.24



Effect of Mixing Temperature on Red Shoe sole

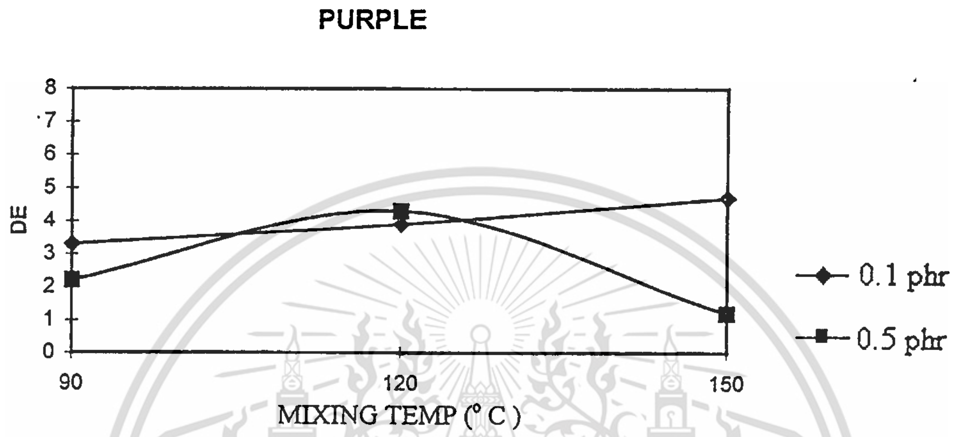
Fig. 23 also shows effect of mixing temperature on DE value for two different concentrations of colour masterbatch (0.1 and 0.5 phr). It can be seen that the DE value of 0.1 phr red rubber band formulae changed dramatically as the mixing temperature increase. On contrary, small change of DE value for high concentration of red colour can be found up to 120° C. However, beyond mixing temperature of 120° C DE value increase with increasing temperature. This shows that although using high concentration the DE can be affected by high mixing temperature.

The DE value of red shoe sole formulae is shown in Fig.24 which differs from rubber band. The DE of 0.1 phr drops from 9 to 3 units when temperature increases from 90 to 120° C. But in case of 0.5 phr concentration ,the DE is found to be constant at 2.5 units.

When consider the lightness of sample it can be seen from appendix A that the lightness of 0.1 phr Red rubber band are fluctuated from -6.8, -7.1 and 7.7 units and the hue shift to yellow/green side by

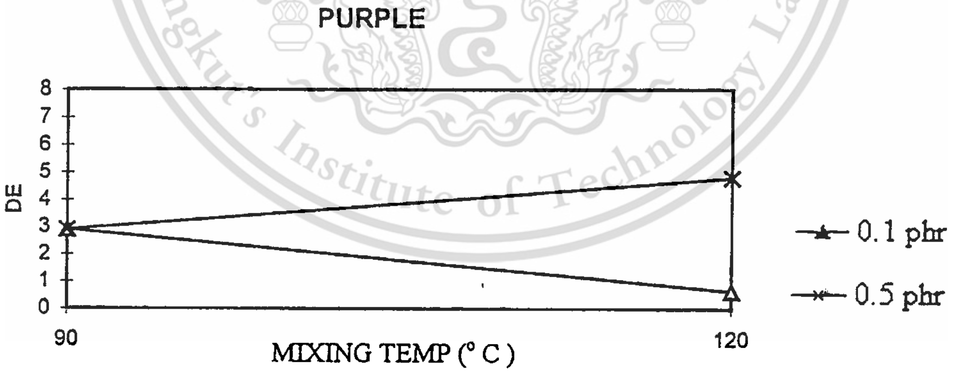
6.2, 6.5 and 4.5 units when mixing temperature increase to 90°, 120° and 150° C.

Fig.25



Effect of Mixing Temperature on Purple Colour Rubber band

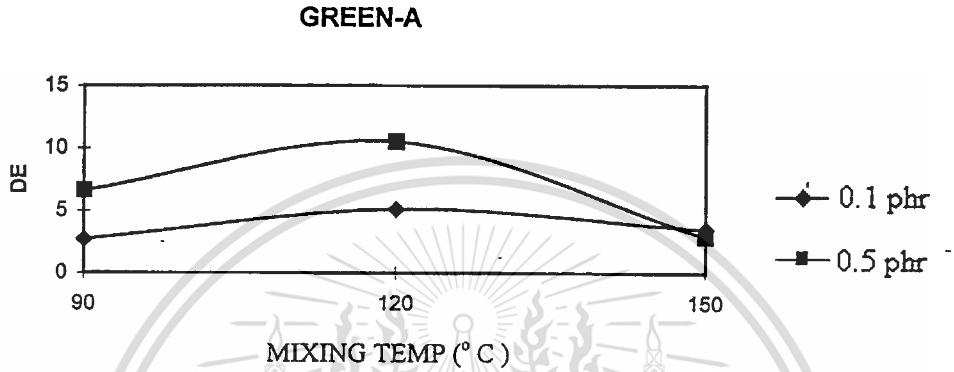
Fig.26



Effect of Mixing Temperature on Purple Colour Shoe sole

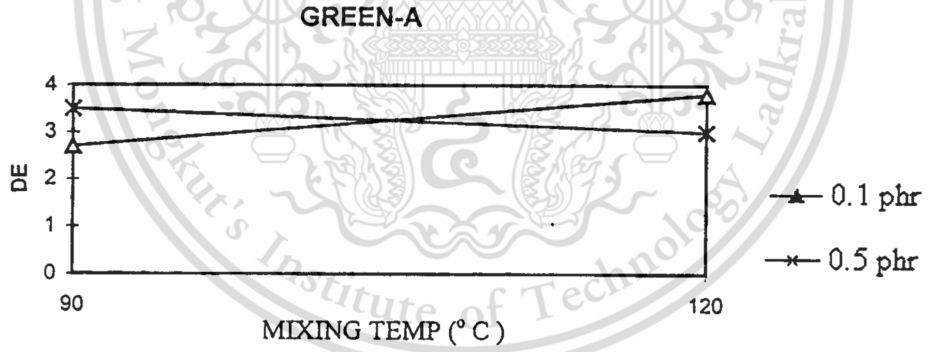
Rubber band with 0.1 and 0.5 phr of purple colour masterbatch (Fig. 25) has a small DE. This colour shows a good dispersion. Thus it cannot be seen any difference in colour by visual. The changing in DE come from a yellowish form of rubber itself. Also the same as shoe sole formulation.

Fig.27



Effect of Mixing Temperature on Green-A Colour Rubber band

Fig.28



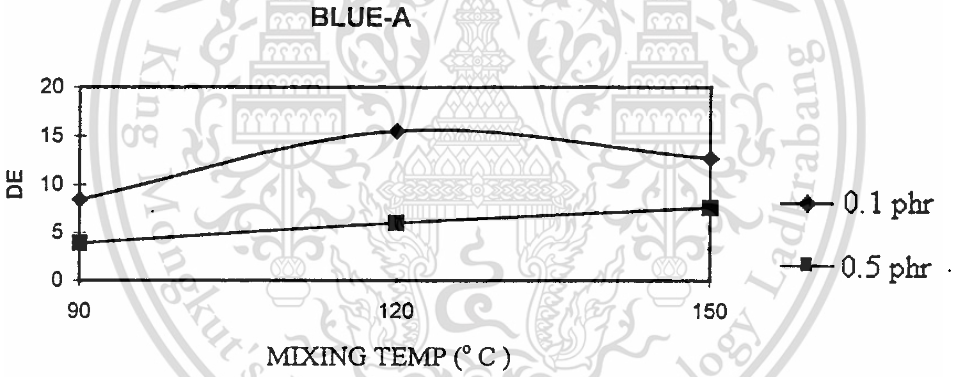
Effect of Mixing Temperature on Green-A Colour Shoe sole

The 0.1 phr. Green-A colour of rubber band shows colour difference raise from 2 to 5 units with increasing mixing temperature from 90° to 150° C. The lightness changes from -1.4, 2.1 and 0.7 units when mixing temperature raised to 90°, 120° and 150° C. However, the hue is found to be constant at 1.9 units to yellow/red side for both mixing temperature at 120° and 150° C.

For 0.5 phr Green-A rubber band show DE from 6.6, 10.5 and 2.9 units. The lightness value changes by 1.9, 3.6 and -1.6 units while the hue shift to green/blue side by 2.7, 6.9 and 1.1 units with corresponding to mixing temperature 90°, 120° and 150°C.

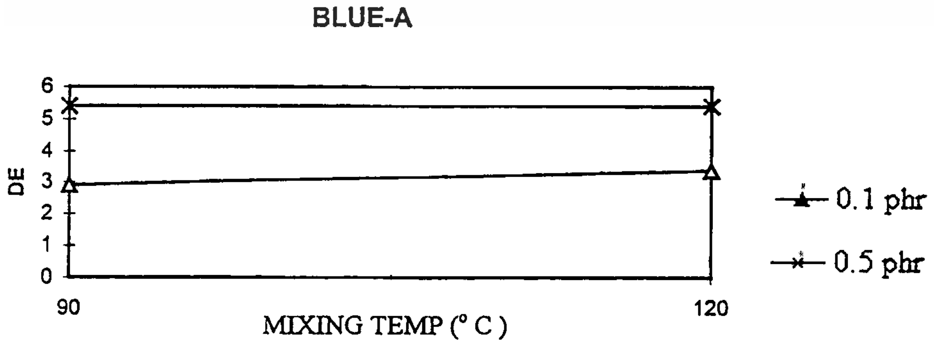
Shoe sole formulae in both concentration show almost constant DE values about 2.7 to 3.9 units. The lightness value is given as -1.7 and -0.3 units. Hue shifts to green/blue side by 2 units and to yellow/red side by 0.4 units corresponding to mixing temperature at 90° and 120°C.

Fig.29



Effect of Mixing Temperature on Blue-A Colour Rubber band

Fig.30



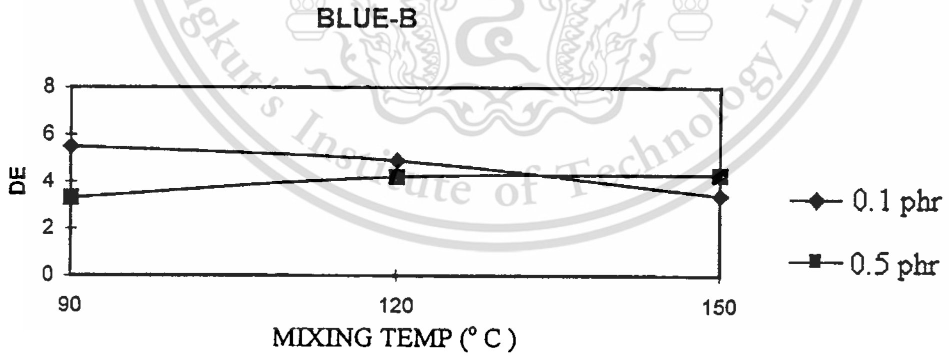
Effect of Mixing Temperature on Blue-A Colour Shoe sole

Fig. 29 show plot of DE with mixing temperature of 0.1 and 0.5 phr Blue-A rubber band. Both concentration have small DE but 0.1 phr show reverse curve at mixing temperature of 150° C. Because of the lightness change from 10.8 to 5.1 units but hue is constant for mixing temperature at 120° and 150° C.

Shoe sole formulae in Fig. 30 show constant DE. Thus small change of lightness can be found. For 0.1 phr Blue-A shoe sole change only 0.1 unit from -2.3 to -2.4 units with mixing temperature increase from 90° to 120° C. The hue shift from blue/red side by 0.9 unit and, with increasing temperature, to green/yellow side by 2 units.

The 0.5 phr Blue-A shoe sole show small change in lightness 3.3 to 4.6 units and hue change from 3.1 to 2 units in green/yellow side.

Fig.31



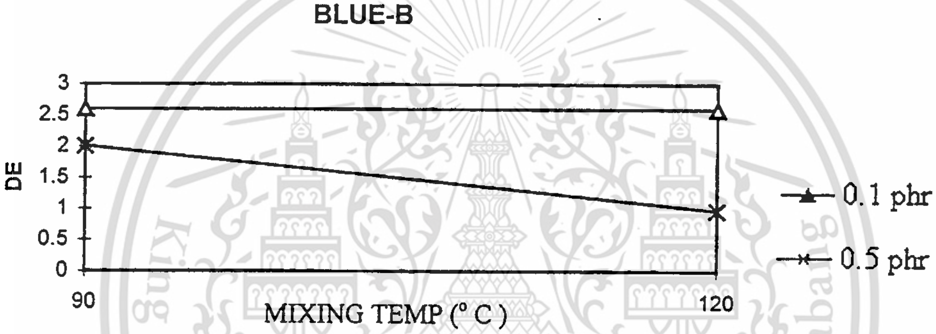
Effect of Mixing Temperature on Blue-B Colour Rubber band

Fig. 31 show 0.1 and 0.5 phr Blue-B rubber band. The DE of 0.1 phr rubber band drop from 5.5 to 7.9 and 3.4 units with corresponding to mixing temperature of 90°, 120° and 150° C. When consideration of the lightness from appendix A it can be seen that the lightness changes

0.4, 3.1 and 2.1 units and hue shift to blue/red side by 4.9 and 3.8 units and at the temperature above 120° C to green/yellow by 1.9 units.

The 0.5 phr Blue-B rubber band the lightness change from -2.5 units to 1.3 units and then decrease to -2.9 units at mixing temperature 90°,120° and 150° C. The hue shift to red/yellow side by 0.6, 0.8 and 1 unit.

Fig.32



Effect of Mixing Temperature on Blue-B Colour Shoe sole

It can be seen from Fig. 32 that 0.1 phr Blue-B shoe sole formulation show DE constant at 2.6 units while 0.5 phr Blue-B DE drop from 2 to 0.98 units.

However the DE value of 3-5 units in both formulations represented small different by visual. The colour difference may arise from the degradation of rubber.

The Cure Temperature and Cure Time

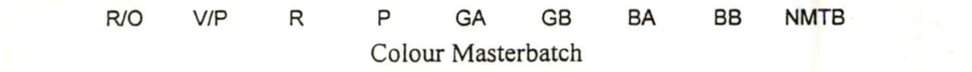
Because of safety precaution, the rubber product always vulcanises and attains at time to 90% of maximum torque (t_{90}). Beyond

t_{90}, the rubber sample might be over cure and desulphurisation can be dominated. Therefore, a standard or reference sample was cured to t_{90} while others samples were cured at t_{70} and t_{110} in order to investigate the effect of cure time, cure temperature and chemistry of vulcanisation simultaneously.

The samples were vulcanised using cure time shown in Table 9. The compound with good dispersion mixed at 40°C was selected for vulcanisation.

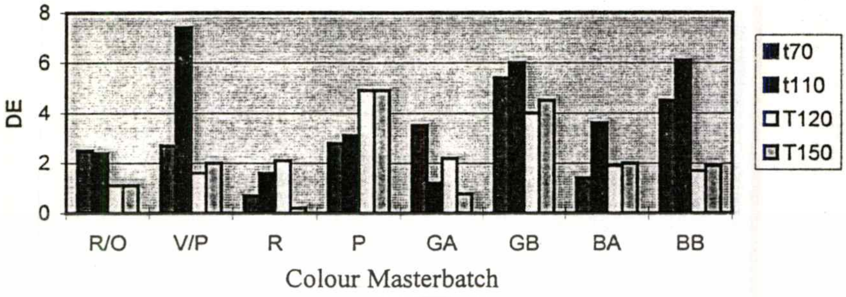
It can be seen form Figs. 33-34 that the colour difference of t_{70} (under cure) and 110% crosslinking (over cure) are also difference from standard sample. Thus, the colour of product must be cured at same extent of crosslinking in order to obtain the same colour shade.

Fig.33



Effect of Crosslinking and Cure temperature on Colour Difference (DE) of 0.1 phr Coloured Rubber band

Fig.34

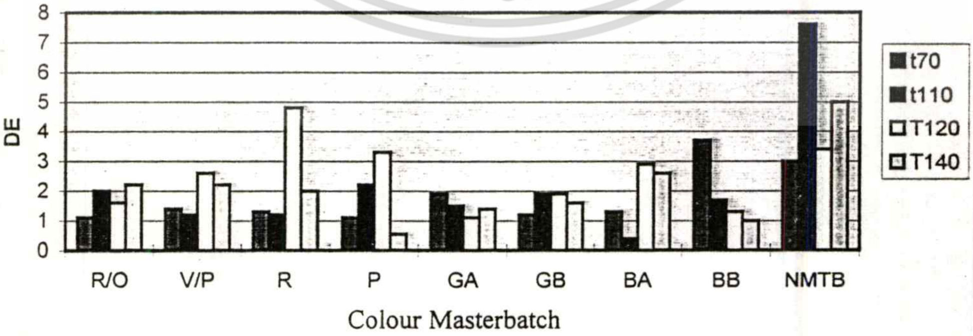


Effect of Crosslinking and Cure temperature on Colour Difference (DE) of 0.5 phr Coloured Rubber band

The symbolic used in the graph are shown as follow :-

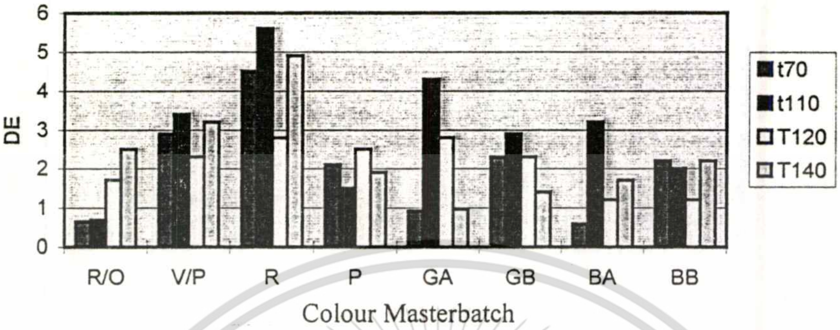
t70 = under cure
t110 = over cure
T120 = Cure temperature at 120° C
T150 = Cure temperature at 150° C

Fig.35



Effect of Crosslinking and Cure temperature on Colour Difference (DE) of 0.1 phr Coloured Shoe sole

Fig.36



Effect of Crosslinking and Cure temperature on Colour Difference (DE) of 0.5 phr Coloured Shoe sole

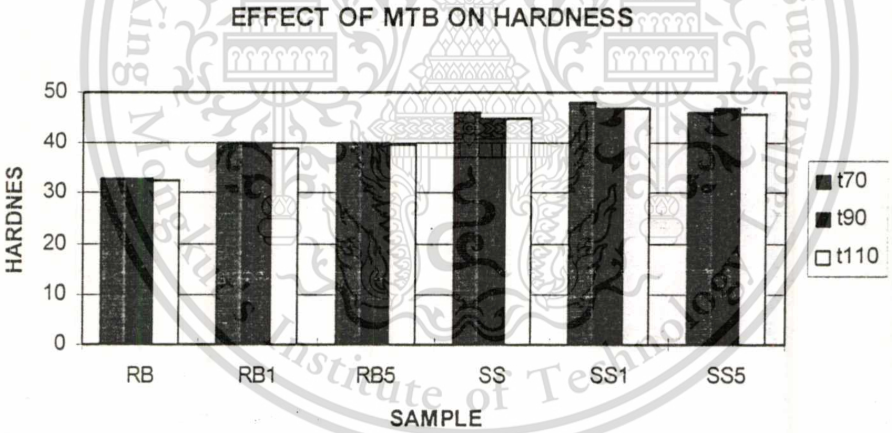
Thus, it can be observed from Figs. 33-36 that the suitable cure temperature for each formulation is also affected to colour difference.

For the rubber band formulation cure temperature used is 140° C. If lower cure temperature to 120° C, the cure time increases to 45 min. Thus, time for a possible interaction between the pigments and the other components of the formulation at activated temperature is also longer. The colour may be changed with same crosslinking. The same as high cure temperature with shorter time in the mould. The interaction of colour and components may be shorter. The colour shade can also be changed from the standard.

Effect of Masterbatch on Hardness

For shoe sole and rubber band, one of the physical property which always being measured is hardness. According to Fig. 35, the hardness of samples for both formulations are in the same tolerance value. It shows a little increase when colour masterbatch were added. Thus, it is found no such significant effect on this type of property. The hardness of under cure and over cure are also found to have not much difference from standard.

Fig.37



Effect of colour masterbatch on hardness of rubber band and shoe sole

RB = Rubber band
RB1 = Rubber band with 0.1 phr colour pigment
RB5 = Rubber band with 0.5 phr colour pigment
SS = Shoe sole
SS1 = Shoe sole with 0.1 phr colour pigment
SS5 = Shoe sole with 0.5 phr colour pigment
t70 = under cure at 70%
t90 = standard cure at 90%
t110 = over cure at 110%

Effect of Chemicals

A possible interaction between the colourants and the other components of the formulation such as accelerators ,activators or rubber itself are believed to cause the discolouration. It can be clearly seen from same chemical group can be formed when mixing at activated temperature. However, the colour masterbatches which were used in this study are, actually, the mixtures of many pigments. The chemical structure becomes complicated. Thus, enhancing a high tolerance to high processing temperature too.

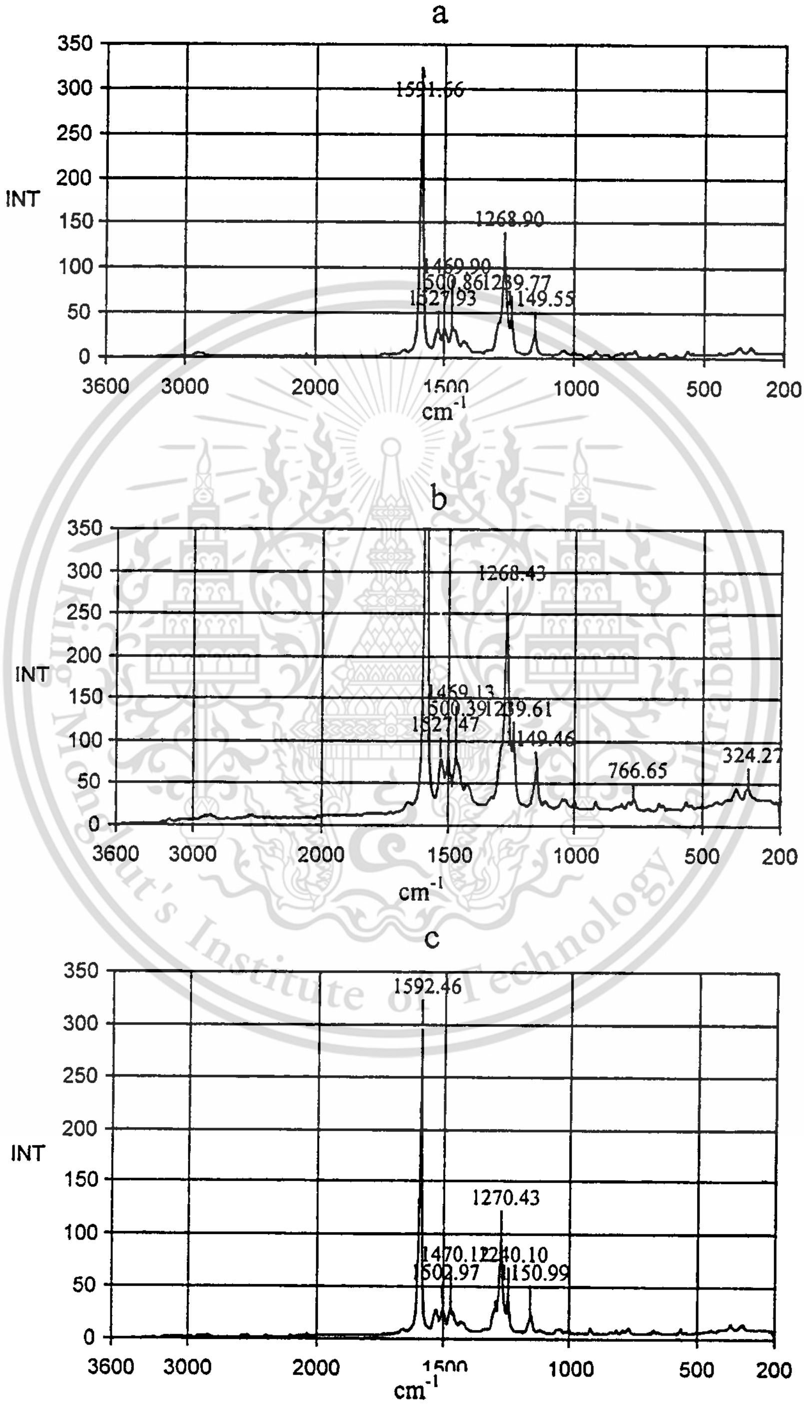
The FT-Raman spectrum of red/orange colour masterbatch mixed with accelerators for rubber bands and shoe sole are shown in Figs.37 and 38.

For investigation of chemical interaction between colour masterbatch and accelerators, the FT-Raman measurement was employed. Spectrum of samples which were annealed at temperatures of 120 and 150° C (for cure time of rubber band and shoe sole at 120 and 150° C) were illustrated in Figs. 38 and 39 (a-c).

The technique used was a modern conventional laser-Raman systems for recording spontaneous Raman spectra comprise essentially an appropriate source, some dispersing and collection optics and a sensitive detector. The comparative simplicity of sampling that Raman measurement offers to many investigations e.g. minimal preparation or direct analysis , or use of glass containers, now coupled with the capability FT-Raman brings of mostly avoiding intense fluorescence emissions, will help to popularise Raman measuments in many more industrial, research and investigative laboratories. (B.J.Hunt and M.I.James 1993:72-73)

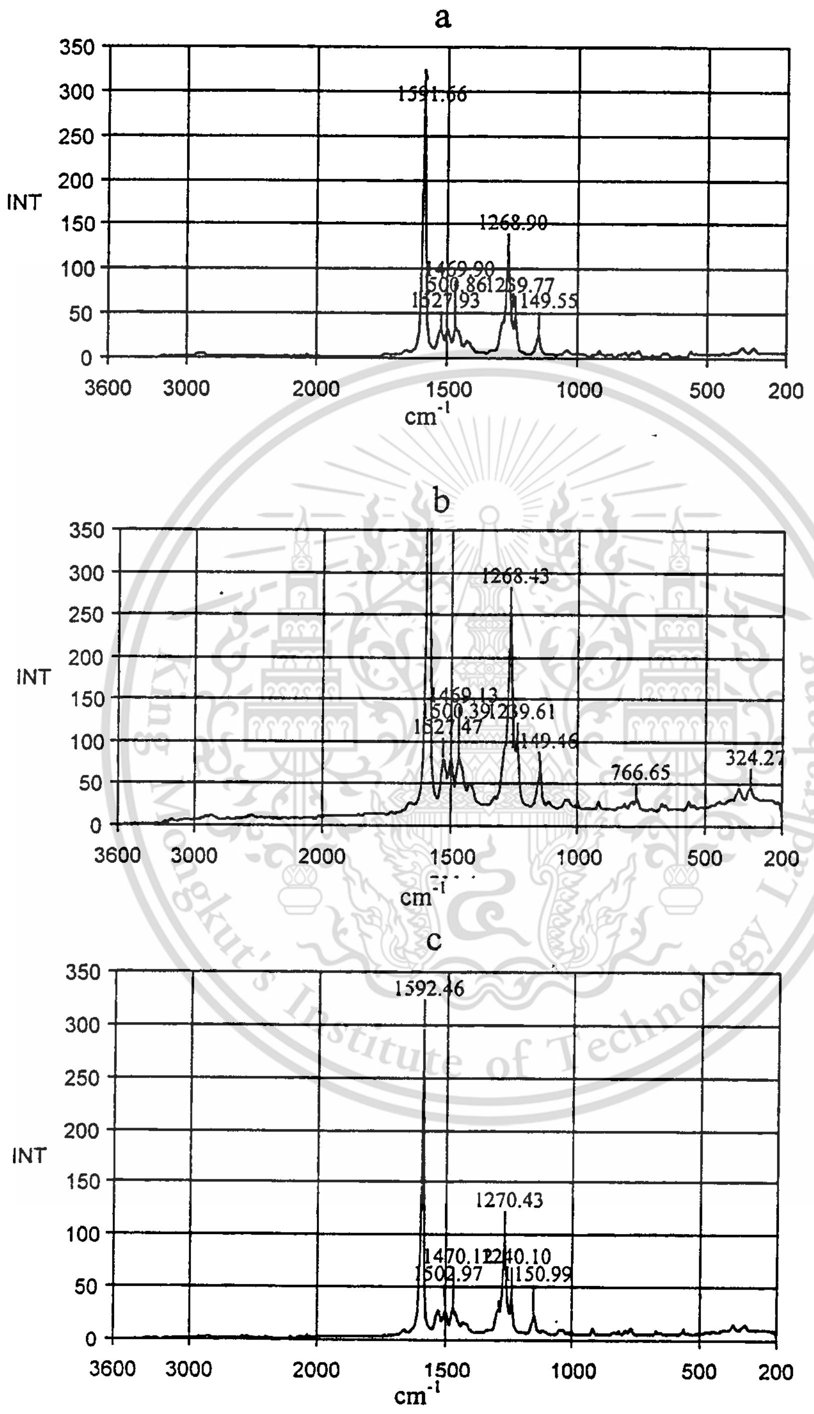
It can be seen from Figs. 38 to 39 that spectrums of annealed samples at 120° and 150° C show similar peaks to that of sample at room temperature. The peaks at 1591,1502 and 1270 cm^{-1} represent C-H stretching of aromatic, phenyl and C-N respectively. It is recognized that colour masterbatch is a combination of organic colour and can be tolerance to high temperature of nearly 200° C. Therefore, no evidence of chemical changed can be found in colour masterbatch sample mixed with accelerator, activators at elevated temperature.

Fig.38



FT-Raman Spectrum of CBS and TMTD mixed with red/orange colour masterbatch a. Room Temp. b. 120° C c. 150° C

Fig.39



FT-Raman Spectrum of MBTS and TMTM mixed with red/orange colour masterbatch a. Room Temp. b. 120° C c. 150° C

Chapter 5

Conclusion

From this study, it can be seen that the chemicals and process variables are affected the colour appearance of rubber products used for this study ,i.e., elastic rubber band and shoe sole.

The samples of both formulations were prepared in various conditions and colour difference was measured between standard and batch by ICS-Texicon colour system. The DE value can be obtained from CIE L*a*b* equation with D65 illuminant and the accepted value is less than 0.5.

The effect of mixing temperature was found to be an important variable for the colour difference. The high mixing temperature (more than 120° C) can affect the dispersion of pigments and cause degradation of NR.

From this study it can be concluded as follows :-

1. It was found that the mixing temperature was a major effect of colour fading.

2. It can be seen that the colour of rubber product will be changed upon the process variables changed, for example, cure temperature, cure time (over cure and under cure).

3. It was found that low masterbatch concentration showed higher DE value than that of high masterbatch concentration. This implies that

using high concentration can reduce cause of colour fading but it can increase production cost.

4. The high mixing temperature was found to be able to degrade NR and formed dark yellowish colour. The pigment was also found difficult to disperse when mixed at high temperature.

5. It was found that the dispersibility of colour masterbatch was depended on the chemical structure and type of pigments.

6. The chemicals in formulations such as accelerators can react with rubber molecules at high mixing temperature which may lead to colour changing of rubber matrix.

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Appendix A

Table 14
Colour Difference Data

ICS-TEXICON colour system
CIEL*a*b* equation
D65-10' illuminant

A. Mixing temperature

ROTOR 60 RPM
NR WT 40 G

RUBBER BAND CURE 140 C 15 MIN

MTB	TEMP	MAST	MIX	NMTB	R/O	V/P	R	P	G-A	G-B	B-A	B-B
0.1	40	3	5	REF	REF	REF	REF	REF	REF	REF	REF	REF
	90	3	5	4.6	21.9	4.7	20.3	3.3	2.7	11.8	8.4	5.5
	120	0.5	3	5	25.2	5.1	24.0	3.9	5.1	35.3	15.5	4.9
	150	0.5	3	7.4	30.9	4.2	16.9	4.7	3.5	45.7	12.7	3.4
0.5	40	3	5		REF	REF	REF	REF	REF	REF	REF	REF
	90	3	5		7.6	6.8	3.8	2.2	6.6	11.0	3.9	3.3
	120	0.5	3		8.5	10.0	1.8	4.3	10.5	17.2	6.0	4.2
	150	0.5	3		20.2	5.0	13.0	1.2	2.9	11.2	7.6	4.3

SHOE SOLE CURE 150 C 8 MIN

MTB	TEMP	MAST	MIX	NMTB	R/O	V/P	R	P	G-A	G-B	B-A	B-B
0.1	40	3	5	REF	REF	REF	REF	REF	REF	REF	REF	REF
	90	3	5	2.9	9.1	4.4	7.1	2.9	2.7	5.3	2.9	2.6
	120	0.5	3	2.7	14.3	4	6	0.63	3.8	5.3	3.4	2.6
	150	0.5	3	4.9								
0.5	40	3	5		REF	REF	REF	REF	REF	REF	REF	REF
	90	3	5		12.5	1.1	2.5	2.9	3.5	14.2	5.4	2
	120	0.5	3		18.5	4.2	2.2	4.8	3	17.4	5.4	0.98
	150	0.5	3									

B. Cure temperature and cure time

RUBBER BAND

MTB	TEMP	t	TIME	NMTB	R/O	V/P	R	P	G-A	G-B	B-A	B-B
0.1	120	t90	45	6.7	2.9	2.2	9.2	2.8	11.3	5.2	6.3	3
	140	t90	15	REF	REF	REF	REF	REF	REF	REF	REF	REF
	150	t90	5.8	4.4	3.4	3.3	6.7	2.2	11.1	6.2	6.5	3.5
	140	t70	12.4	2.6	3.8	2.3	4.4	4.4	7.8	6.2	5.2	2.8
	140	t90	15	REF	REF	REF	REF	REF	REF	REF	REF	REF
	140	t110	17.6	6.9	4.1	2.3	7	4.3	9.3	3.5	7.1	3
0.5	120	t90	45		1.1	1.6	2.1	4.9	2.2	4	1.9	1.7
	140	t90	15		REF	REF	REF	REF	REF	REF	REF	REF
	150	t90	5.8		1.1	2	0.2	4.9	0.76	4.5	2	1.9
	140	t70	12.4		2.5	2.7	0.69	2.8	3.5	5.4	1.4	4.5
	140	t90	15		REF	REF	REF	REF	REF	REF	REF	REF
	140	t110	17.6		2.4	7.4	1.6	3.1	1.2	6	3.6	6.1

SHOE SOLE

MTB	TEMP	t	TIME	NMTB	R/O	V/P	R	P	G-A	G-B	B-A	B-B
0.1	120	t90	57	3.4	1.6	2.6	4.8	3.3	1.1	1.9	2.9	1.3
	140	t90	15.7	5	2.2	2.2	2	0.55	1.4	1.6	2.6	1
	150	t90	8	REF	REF	REF	REF	REF	REF	REF	REF	REF
	150	t70	7.7	3	1.1	1.4	1.3	1.1	1.9	1.2	1.3	3.7
	150	t90	8	REF	REF	REF	REF	REF	REF	REF	REF	REF
	150	t110	10.4	7.6	2	1.2	1.2	2.2	1.5	1.9	0.4	1.7
0.5	120	t90	57		1.7	2.3	2.8	2.5	2.8	2.3	1.2	1.2
	140	t90	15.7		2.5	3.2	4.9	1.9	0.96	1.4	1.7	2.2
	150	t90	8		REF	REF	REF	REF	REF	REF	REF	REF
	150	t70	7.7		0.65	2.9	4.5	2.1	0.91	2.3	0.59	2.2
	150	t90	8		REF	REF	REF	REF	REF	REF	REF	REF
	150	t110	10.4		0.69	3.4	5.6	1.5	4.3	2.9	3.2	2

C. Rubber band with various mixing temperature

	MTB CONC.=0.1 PHR						MTB CONC.=0.5 PHR					
TEMP	L	a	b	C	H		L	a	b	C	H	
R/O												
REF	41.6	42.8	24.2	49.2	29.4		37.4	36.2	14.9	39.1	22.4	
90	12	-14.1	11.7	-3.3	18	YG	4.6	1.8	5.8	4.1	4.5	YG
120	14	-15.1	12.3	-4.5	20.5	YG	7.8	-0.6	3.4	0.9	3.3	YG
150	16	-23.3	12.6	-7.6	25.4	YG	13	-6.1	14.2	2.8	15.3	YG
V/P												
REF	41.2	37.7	13.3	40	19.5		41.3	32.6	5.9	33.1	10.3	
90	3.2	1.7	3	2.7	2.2	YG	-4.6	1.1	4.9	2.3	4.5	YG
120	5.1	0.3	0.7	0.5	0.6	YG	-2.6	6.4	7.2	8	5.4	YG
150	1.1	1.8	3.6	3	2.7	YG	-3	-1.1	3.9	-0.1	4	YG
R												
REF	51.9	31	11.7	33.1	20.7		38.4	37.8	16.4	41.2	23.4	
90	-6.8	13.6	13.4	18.1	6.2	YG	-0.1	-3.1	-2.2	-3.7	0.8	RB
120	-7.1	16.9	15.4	21.9	6.5	YG	0.9	1.5	0.4	1.6	0.2	RB
150	7.7	11.3	10	14.4	4.5	YG	2.9	-10	-7.8	-12.1	3.8	RB
P												
REF	33.1	6.1	-6.2	8.7	314.4		29.5	2.5	-4.3	5	300.1	
90	-2.5	2	-0.6	1.9	0.9	RY	-1.7	-0.7	1.3	-1.5	0.1	RY
120	-1.3	2.9	-2.3	3.7	0.4	RY	1.3	2.7	-3.2	4.1	0.5	RY
150	-2.6	2.3	3.2	0.2	3.9	RY	0.7	0.1	1	-0.8	0.6	RY
G-A												
REF	41.7	-32.3	12.8	34.8	158.4		34	-15.9	1.6	16	174.3	
90	-1.4	1.8	-1.4	-2.2	0.6	GB	1.9	5.7	-2.7	-5.8	2.7	GB
120	2.1	-3.2	3.4	4.3	1.9	YR	3.6	8	-5.8	-7	6.9	GB
150	0.7	3.3	0.7	-2.8	1.9	YR	-1.6	2.1	-1.2	-2.2	1.1	GB
G-B												
REF	40.6	-30.3	14.7	33.6	154.1		46.3	-27.7	13.1	30.6	154.6	
90	5.6	10.3	1.5	-7.9	6.7	YR	-7.7	6.4	-4.5	-7.7	1.6	GB
120	16.5	26.9	15.8	-2.9	31.1	YR	-2.5	15.6	-6.6	-16.9	1	YR
150	21.3	32.7	4.9	4.9	40.1	YR	-4.7	9.7	-3	-10.1	1.8	YR
B-A												
REF	32.3	-11.5	-7.1	13.5	211.6		31.3	-4.5	-10.5	11.4	246.8	
90	2.9	-5.7	5.5	3.8	6.9	GY	-0.7	2.3	3.1	-3.7	1.1	BR
120	10.8	-6.4	9	4.5	10.1	GY	3.4	3.1	3.8	-4.6	1.8	BR
150	5.1	-7.7	8.8	5.8	10.1	GY	6.2	3.6	2.6	-3.4	2.8	BR
B-B												
REF	31.7	-11.5	-7.5	13.8	212.9		32.7	1.2	-13.1	13.2	275.4	
90	0.4	5.1	1.9	-2.4	4.9	BR	-2.5	0.3	2.1	-2.1	0.6	RY
120	3.1	2.6	2.8	-0.2	3.8	BR	1.3	0.3	4	-3.9	0.8	RY
150	2.1	0.8	2.5	-1.9	1.9	GY	-2.9	0.6	3.1	-3	1	RY

D. Shoe sole with various mixing temperature

	MTB CONC.=0.1 PHR						MTB CONC.=0.5 PHR					
TEMP	L	a	b	C	H		L	a	b	C	H	
R/O												
REF	44.4	23.8	11.4	26.4	25.6		38.3	30.7	12.1	33	21.5	
90	5.4	-6.3	3.7	-3.3	6.5	YG	9.2	-8.4		-7.7	3.5	YG
120	11	-3.9	8.3	1.6	9	YG	13.6	-12.2	3	-9.1	8.7	YG
V/P												
REF	48.5	25.2	8.2	26.5	18		43.4	25.7	0.6	25.7	1.4	
90	-2.7	3.1	1.4	3.4	0.4	YG	-1	0.4		0.4		
120	-1.4	2.1	3.2	1.3	3.6	RB	-2.8	3	-0.7	3	0.8	RB
R												
REF	46.8	31.7	19.3	37.2	31.3		40.4	31.7	12.8	34.2	21.9	
90	-3.3	-5.2	-6.2	-7.6	2.9	RB	0.1	2.2	1.1	2.5	0.2	YG
120	2.1	-1.1	-1.5	-1.7	0.7	RB	-0.4	2	-0.8	1.6	1.5	RB
P												
REF	38	6.9	-8.4	10.9	309.4		31.4	7	-12.3	14.2	299.7	
90	-0.6	-0.3	2.8	-2.3	1.7	RY	-1.8	-1	2.1	-2.3	0.2	RY
120	0.59	-0.09	-0.19	0.09	0.19	BG	4.3	-2	0.8	-1.6	1.4	BG
G-A												
REF	45.9	-20.6	5.5	21.3	165		37.7	-18.2	-0.3	18.2	180.9	
90	-1.7	0.2	-2.1	-0.6	2	GB	1.8	2.9	-0.9	-2.8	1.1	BR
120	-0.3	3.7	-0.6	-3.7	0.4	YR	2.6	1.4	0.6	-1.4	0.6	GY
G-B												
REF	54.5	-14.1	-12.3	16.6	110.4		42.8	-16.4	2.2	16.5	172.4	
90	-10.5		-0.4	3.6	18.4	GB	7.1	9.3	8	-4.1	11.6	YR
120	-2.9			-0.4	0.2	GB	10.3	11.4	8.2	-5	13.1	YR
B-A												
REF	40.8	-10.4	-7.3	12.7	215.2		33.9	-2.7	-16.1	16.4	260.5	
90	-2.3	1.7	0.2	-1.4	0.9	BR	3.3	-2.2	3.6	-2.9	3.1	GY
120	-2.4		2.4	-1.3	2	GY	4.6	-1.5	2.4	-2	2	GY
B-B												
REF	39.2	-8.4	-11.3	14.1	233.4		34.8	-1.2	-15.5	15.6	265.7	
90	-1.9	0.7	-1.7	1	1.5	BR	-0.8	-0.9	-1.6	1.7	0.7	GY
120	0.2	0.3	2.5	-2.2	1.4	GY	-0.13	0.01	-0.97	0.97	0.08	BR

Biography

Mr.Wason Jaitrongkla was born on the 28th of August,1967 at Petchaboon. He received his B.Sc.(Chemistry) from Chiang Mai University in 1988. Then he was appointed in a position of process controller at Thai Peroxide Co., Ltd. from 1988-1989. At present, he has joined Royal Thai Army as production officer for Explosive Filling Plant, Artillery Ammunition Plant, Army Weapon Production Center (AWPC). His latest rank is a Captain.