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PREPARATION OF OPEN CELL SPONGE RUBBER FOR PRINTING APPLICATION

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งานวิจัยนี้ทำการศึกษายางฟองน้ำเซลล์เปิดโดยใช้เทคนิคการชะเกลือออกจากเนื้อยาง โดยใช้ยางไนไทรล์บิวทะไดอีนที่มีปริมาณอะคริโลไนไทรล์ 40 เปอร์เซ็นต์มาผสมกับส่วนผสมของสารที่ทำให้เกิดวัลคาไนเซชันและผงเกลือที่สามารถละลายน้ำได้ คือ โซเดียมคลอไรด์และโซเดียมไนเตรต ทำการผสมยางด้วยเครื่องบราเบนเดอร์และเครื่องผสมสองลูกกลิ้ง ใช้สารลดแรงตึงผิวประเภทแอนไอออนิกและนอนไอออนิกผสมเพื่อช่วยในการล้างเกลือออกจากเนื้อยาง ติดตามสมบัติของยางคอมพาวด์ที่ได้โดยทดสอบสมบัติของยางวัลคาไนเซชัน น้ำหนักเกลือที่ออกจากเนื้อยาง ความแข็งของยางฟองน้ำ การดูดซับหมึก และการทดสอบรอยพิมพ์ รวมทั้งศึกษาโครงสร้างเซลล์เปิด คุณสมบัติความแข็งขึ้นอยู่กับชนิดและปริมาณของคาร์บอนแบล็ค ขนาดและปริมาณของเกลือโซเดียมไนเตรตสามารถสร้างรูพรุนเซลล์เปิดได้แต่เกิดเซลล์เชื่อมต่อไม่เพียงพอ ส่วนผสมยางฟองน้ำที่เหมาะสมที่สุดสำหรับการใช้เกลือโซเดียมไนเตรตอย่างเดียว คือ สูตร 5 (โซเดียมไนเตรตขนาด 100 เมช) ส่วนระบบโซเดียมคลอไรด์ผสมสารลดแรงตึงผิวประเภทไม่มีประจุ คือ สูตร 9 (โซเดียมคลอไรด์ผสมอีมานอน) เป็นสูตรที่มีประสิทธิภาพมากที่สุดในการเตรียมยางฟองน้ำรวมทั้งให้คุณภาพรอยพิมพ์ที่ดีและสามารถขึ้นรูปตัวอักษรได้

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต ยุพาภรณ์ รถทอง
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In this research, sponge rubbers having numerous open cells were prepared by salt leaching technique. The nitrile butadiene rubber (NBR) with 40% acrylonitrile was compounded with vulcanization ingredients, and fine powder of water-soluble salts: sodium chloride and sodium nitrate. The compounding process was performed by using a Brabender and two-roll mill filled with various types of anionic and nonionic surfactants, which were used in order to wash out the salts from the rubber composites. The following properties of all rubber compounded samples were determined; cure characteristic, removal weight of sodium salt, hardness of sponge rubber, ink adsorption and impression test. The hardness property depended on carbon black types and contents and particle size of salts and contents. $NaNO_3$ could also form the open cell but the pore interconnection was not enough. The optimal recipe sponge rubber composition for $NaNO_3$-based porosity formation is formula 5 (100 mesh $NaNO_3$). Whereas system of NaCl was blended with the surfactant, nonionic surfactant as formula 9 (NaCl mixed Emanon), was the most effective recipe to prepare the porous rubber, giving the best imprint quality and pressed character surface.

Field of study..Petrochemistry and Polymer Science.. Student's signature.......................
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CONTENTS

PAGE

PAGE

LIST OF TABLES

TABLES **PAGE**

TABLES **PAGE**

TABLES **PAGE**

LIST OF FIGURES

FIGURES **PAGE**

FIGURES **PAGE**

FIGURES **PAGE**

FIGURES **PAGE**

FIGURES **PAGE**

FIGURES **PAGE**

LIST OF ABBREVIATIONS

NBR : Nitrile butadiene rubber
SBR : Styrene butadiene rubber
phr : Parts per hundred of rubber
MBTS : Mercaptobenzothiazole disulfide
DPG : Diphenyl guanidine
DOP : Dioctyl(2-ethylhexyl) phthalate
NaCl : Sodium chloride
$NaNO_3$: Sodium nitrate
MDR : Moving Die Rheometer
SEV : Semi-efficient Vulcanization
ASTM : The American Society for Testing and Material
°C : Degree Celsius
g : gram
h : hour
%wt : Percent by weight

CHAPTER I

INTRODUCTION

Rubber stamping is widely used in many office tasks. Sponge rubber stamps have been used for years long before copying machines and computers. Now, even with the advent of computer technology, they still play a major role in most offices. Authentication of documents cannot be imagined without proper sponge rubber. Today, in addition to natural rubber, synthetic rubber is also widely used.

Butadiene-acrylonitrile copolymer having a nitrile content of 31 to 42% are especially suitable for obtaining products excellent in oil resistance and ageing resistance. Therefore, these copolymers are especially preferred as the starting rubber for a printing sponge rubber material.

Methods for preparing sponge rubbers having numerous open cells, which are used for continuous rotary printing device are following :

(1) A method in which a starting rubber is foamed by using a blowing agent alone to form numerous open cells in the rubber.

(2) A method which uses powder of an easily water-soluble salt, and removing salt by water washing to form numerous open cells in the rubber.

In method (1) open cells formed are not uniform. The resulting sponge material is insufficient in ink-absorbing property. A sufficient amount of an ink cannot be absorbed and stored.

In method (2) fine powder of an easily water-soluble salt does not decompose or gasify at a rubber-curing temperature (110 to 160°C). The salt can be removed easily by washing even after exposure to the curing temperature.

In a typical preparative method, some additives, e.g. sulfur, carbon black and sodium salt are added into the starting rubber, and the resulting mixture is kneaded and milled by an appropriate kneading machine. Then, the kneaded mixture is introduced into a process compression molding. The cured product is taken out from the mold and washed with cold and warm water in the ultrasonic machine. Finally, all the particles contained in the cured product can be completely removed. The cure product was dehydrated and dried.

The current industry uses method (2) in preparing sponge rubber, but a way to develop the preparative method and the property of the sponge rubber is still needed. Some fine powder and easily water-soluble salts can be encountered easily in Thailand and have low cost, e.g. sodium chloride. The properties of sponge rubber can still be further improved by modifying the preparative method.

Therefore, this research was aimed to develop a preparative method to produce sponge rubbers from NBR (acrylonitrile-butadiene rubber) using salt-leaching method. The effects of some additives on the properties of the sponge rubber prepared to have numerous open cells were studied. Finally, the printing quality of the sponge rubbers was also investigated.

Objective of the research

1. To improve a process for producing sponge rubbers having interconnected open cells for continuous rotary printing device.

2. To investigate parameters influencing the properties of the sponge rubbers.
3. To test printing quality using the sponge rubbers produced.

Scope of the research

Methods to produce sponge rubbers by salt-leaching method were experimented. Parameters influencing the property of the sponge rubbers which were studied are: particle size of salts (100, 300 and 400 mesh), content of salts, size and content of carbon black, and type of surfactant (nonionic and anionic). The mechanical, physical properties and characteristics of the compound rubbers were studied by moving die rheometer, hardness shore C and scanning electron microscope (SEM). Removal of sodium salt and adsorption weight of oil ink were determined. The pre-ink stamp was used for quality checking of imprints.

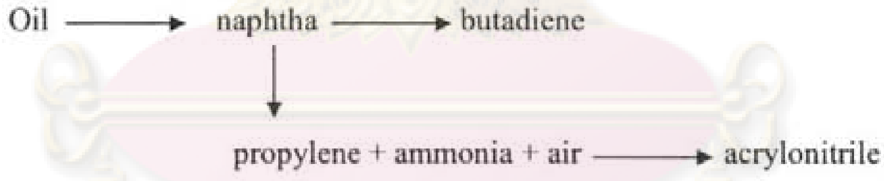
CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Acrylonitrile-butadiene rubber

2.1.1 Production

Acrylonitrile-butadiene rubber (NBR or nitrile rubbers) was manufactured by emulsion copolymerization of butadiene with acrylonitrile in a process similar to those used for other emulsion polymers, such as SBR. The main raw materials required are the monomers, butadiene and acrylonitrile. Both monomers may be synthesized from naphtha.

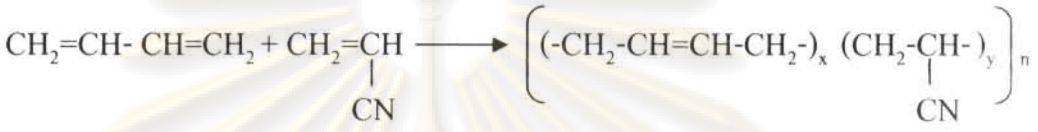


At present, approximately 75% of the world production of acrylonitrile utilizes the Sohio process in which ammonia, propylene, steam, and air are passed through a fluidized bed of finely divided catalyst at about 450-500°C. This and other similar processes are based on the reaction shown below.

$$CH_2=CH-CH_3 + NH_3 + \tfrac{1}{2}O_2 \longrightarrow CH_2=CH-CN + 3H_2O$$

The use of propylene as the basis for the production of acrylonitrile has superseded older routes involving acetylene and hydrogen cyanide, mainly on economic grounds.

In theory, the polymerization reaction can be written as



$$CH_2{=}CH\text{-}CH{=}CH_2 + CH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} \longrightarrow \left[(\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-})_x\ (CH_2\text{-}\underset{\displaystyle CN}{\underset{|}{CH}}\text{-})_y\right]_n$$

The values of n and y depend on the precise polymerization recipe and the temperature of polymerization, it is important to bear in mind that, except under azeotropic conditions, the ratio of the two monomer units in the final polymer will not normally be the same as the ratio in which the monomers were charged into the reaction vessel. As the ratio of butadiene to acrylonitrile in the polymer largely controls its properties, as will be seen later, the design of the polymerization recipe and the temperature at which this is carried out are important features of nitrile rubber production. The properties of the product may be influenced by other details of the recipe, such as the nature and amount of modifiers and emulsifiers.

The early nitrile rubbers were all polymerized at about 25-50°C, and these hot polymers were characterized by their toughness resulting from the presence of a degree of branching of the polymer chains often referred to as 'gel'. By analogy with the development in the emulsion polymerization of SBR, since the early 1950's an increasing number of nitrile rubbers are being produced by 'cold' polymerization at about 5°C, this results in more linear polymers containing little or no gel and which are easier to process than "hot" polymers.

2.1.2 Physical and chemical properties [1]

Nitrile rubbers are classified as specialty rather than general purpose elastomers, as the vulcanized forms are used primarily for their oil, solvent and chemical resistance.

Nitrile rubbers grades available in the marketplace have a 20-50% acrylonitrile content. When properly compounded and cured, the fuel and solvent resistance, abrasion resistance and resistance to gas permeation increase with increasing acrylonitrile content. A second controlled variable in the manufacture of NBR is Mooney viscosity, a measure of average molecular weight ranging in commercial polymers from 30 to 90 arbitrary units. At the low end of this range processability is superior but dynamic mechanical properties may be poorer.

The fluid resistance of compounds containing NBR, as measured by volume swelling in laboratory immersion or by actual performance tests, is proportional to acrylonitrile content, or the polarity imparted by the –CN groups on the polymer chains, and also is a function of the chemical nature of the oil solvent. As a polar rubber, NBR is most resistant to hydrocarbons but is less resistant to polar fluids.

Low temperature behavior is improved as the acrylonitrile content of NBR is reduced. Since oil resistance also declines with reduced acrylonitrile level, the selection if an appropriate NBR type must often involve a compromise depending upon the given service condition.

Two other processes that impart ozone resistance and have assumed commercial importance are blending with poly(vinyl chloride) (PVC) or with ethylene propylene diene elastomer (EDPM). For the former, several commercial blends, containing 30% of dispersed PVC, are available. In compounding, the stiffening influence of PVC is compensated by the use of ester plasticizers.

Other properties of nitrile rubbers can be summarized as shown in Table 2.1.

Table 2.1 The effect of acrylonitrile content on properties of nitrile rubbers [2]

NBR with lower acrylonitrile content		**NBR with higher acrylonitrile content**
	processability	→
	cure rate with sulfur cure system	→
	oil/fuel resistance	→
	compatibility with polar polymers	→
	air/gas impremeability	→
	tensile strength	→
	abrasion resistance	→
	heat-aging	→
←	cure rate w/peroxide cure system	
←	compression set	
←	resilience	
←	hysteresis	
←	low temperature flexibility	

2.1.3 Compounding and vulcanization [3], [4]

The vulcanization systems should be considered before compounding rubber because vulcanization is a process which transforms the plastic material to elastomeric material. Thus, the vulcanization systems are important for rubber compounding and processing. The conventional vulcanization systems always have sulphur as vulcanizing agent, which can crosslink the rubber chains in order to form the rubber network (vulcanized rubber or elastomeric material) illustrated in Figure 2.1. However, vulcanization systems should have activators and accelerators for reducing time of crosslinking.

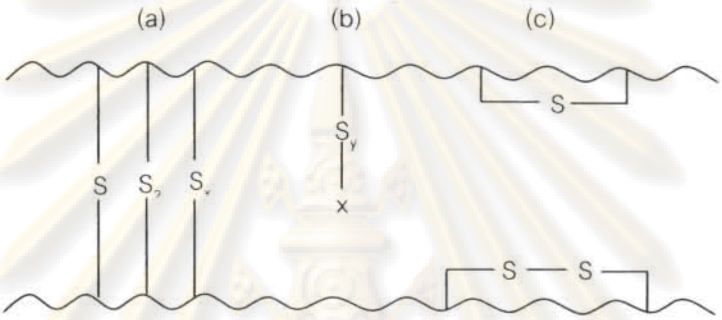


Figure 2.1 Structural features of vulcanizate network [3].

The onset of crosslinking so called scorch time or scorch resistance can be measured by Mooney viscometer (Figure 2.2a). It consists of a rotating disk in a cavity which contains the test rubber. When the time reaches scorch time, the Moony viscosity increase rapidly (Figure 2.2b). The extent and rate of vulcanization are measured by determination of mechanical properties after various cure periods.

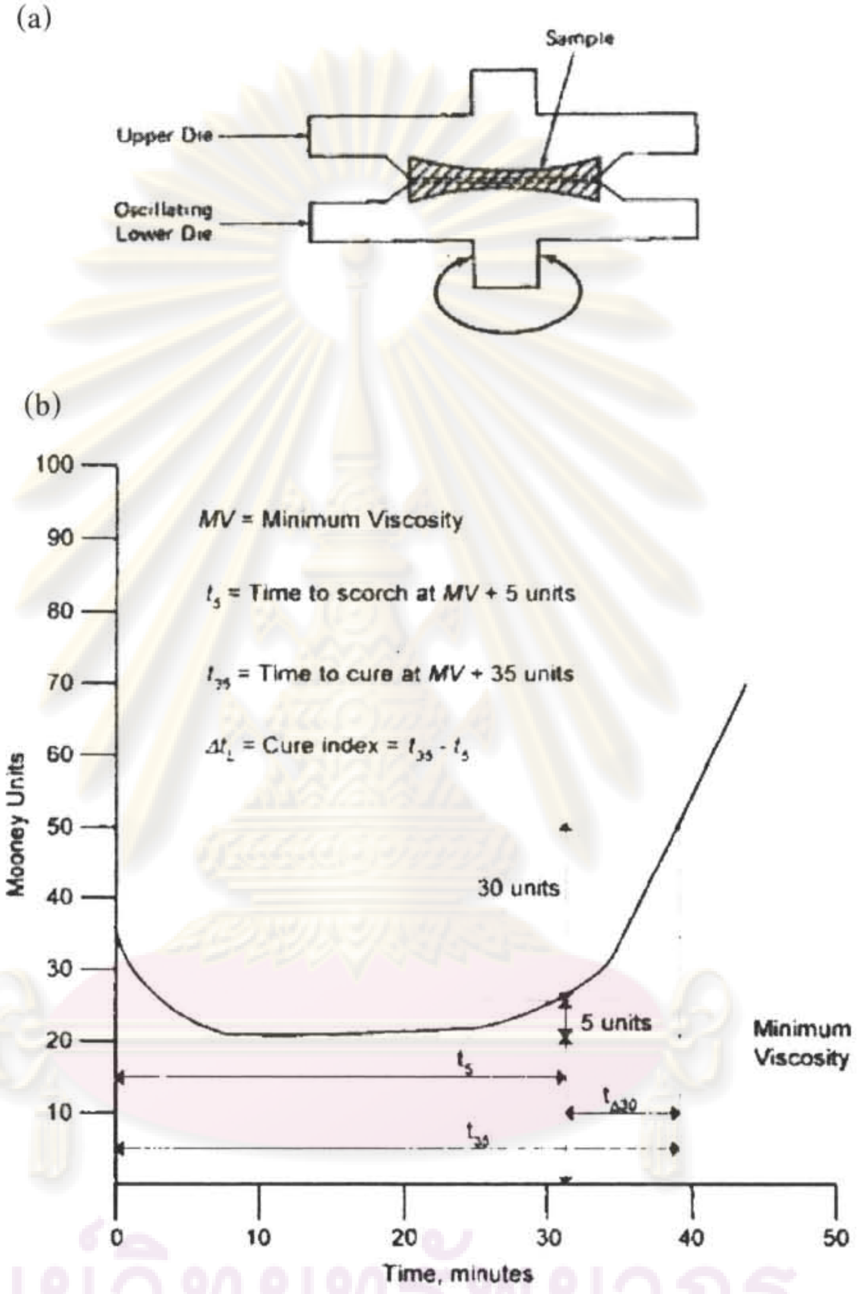


Figure 2.2 [3]

(a) Mooney viscometer.

(b) The effect of scorch on Mooney viscosity.

At present time, rheometer (or cure meter) illustrated in Figure 2.3a is used. This device is capable of measuring the extent of cure of a single sample at a given temperature on a continuous basis as illustrated in Figure 2.3b.

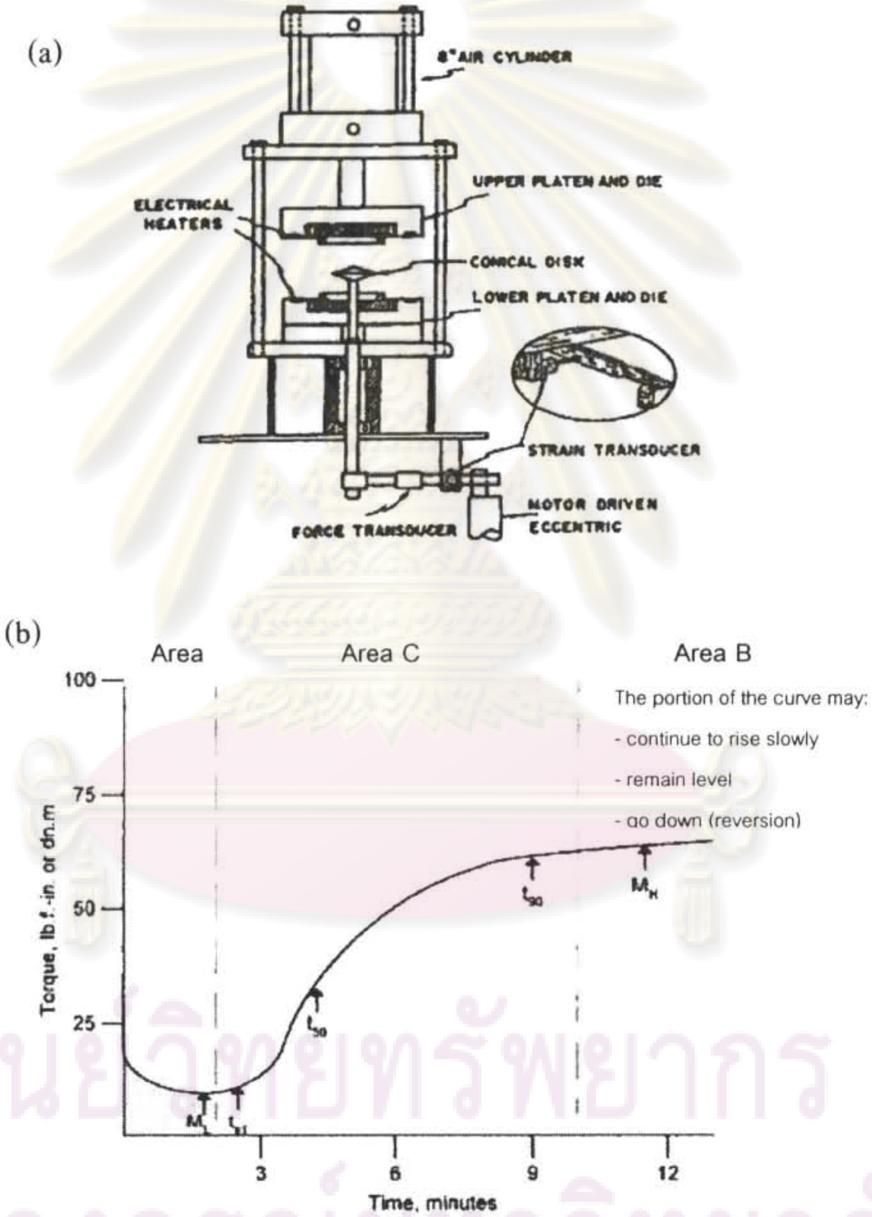


Figure 2.3 [3]

(a) Oscillating disk type curemeter.

(b) Torque cure measured by curemeter.

Generally less sulphur and more accelerator are used with nitrile rubbers than with natural rubber. The most important vulcanizing agents are elemental sulfur and sulfur donors. Organic peroxides are also used as cross-linking agents and they impart good high temperature resistance. Other chemicals that may be required to balance the vulcanization system are activators which reduce the time and temperature requirements for sulfur cure. They include thiazoles, sulfenamides, thioureas, guamidines, dithiocarbamates, thiuram, guanidines, dithiocarbamates, thiuram disulfides, aldehyde-amine reaction products and combination of these. The choice of accelerator is particularly important when compounding for the frequently required low compression set; one such system is TMTD (Tetramethyl Thiuram Disulfide) 3 phr, CBS (N-cyclohexyl-2-benzothaizyl-sulfenamide) 3 phr, sulphur 0.5 phr (parts per hundreds of rubber).

The total compound of polymer, fillers, plasticizer and cure system may be mixed in conventional rubber equipment, such as open mills or internal mixers, then sheeted-off for molding, calendaring or extrusion. Some precautions during these operations are often required to ensure good dispersion of ingredients and to prevent premature cure or scorching of stocks.

Ester and polymeric plasticizers are widely used in NBR because they influence not only processing but also such properties as hardness, low temperature flexibility, and oil resistance. Small quantities of aromatic process oils can occasionally be used, particularly with those NBR types which contain < 30% acrylonitrile.

Nitrile polymers are amorphous, and like SBR, need reinforcement by fillers in order to obtain optimum properties. These fillers may be carbon black or non-black mineral types, the choice depending upon the end use and the requirement of finished products properties. All types of carbon black and non-black fillers may be used with nitrile rubber. Nitrile black masterbatches in a crumb form are commercially available to enable compounders to maintain a clean working environment, with the advantage of shorter mixing cycles [3]. Silica and clays are used where non-black compounds are required, but compression set performance is not so good as a black-reinforced compounds unless silane treated silicas are used.

2.1.4 Applications

Nitrile rubbers are excellent in resistance to oil, chemicals, heat and water, they allow wide applications ranging from oil resistant rubber products to adhesives and PVC blends. They are used in such oil resistance rubber products as oil resistant hoses, packagings, gaskets, diaphragms, shock absorbers, rubber rollers, oil resistant shoe soles, rubber sheets and many other products.

2.2 Surfactant

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups and hydrophilic groups. Therefore, they are soluble in both organic solvents and water.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil.

Surfactants play an important role in many practical applications and products, including: detergents, fabric softener, emulsifiers, paints, adhesives, inks, soil remediation, wetting, ski wax, foaming, defoaming.

Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

Anionic (based on sulfate, sulfonate or carboxylate anions)

- Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and other alkyl sulfate salts
- Sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES)
- Alkyl benzene sulfonate
- Soaps, or fatty acid salts

Cationic (based on quaternary ammonium cations)

- Cetyl trimethylammonium bromide (CTAB)hexadecyl trimethyl ammonium bromide, and other alkyltrimethylammonium salts
- Cetylpyridinium chloride (CPC)
- Polyethoxylated tallow amine (POEA)
- Benzalkonium chloride (BAC)

- Benzethonium chloride (BZT)

Zwitterionic (amphoteric)

- Dodecyl betaine
- Dodecyl dimethylamine oxide
- Cocamidopropyl betaine
- Coco ampho glycinate

Nonionic

- Alkyl poly(ethylene oxide)
- Copolymers of poly(ethylene oxide) and poly(propylene oxide)

2.3 Rubber compounding and processing [4]

2.3.1 Mixing in internal mixers

An internal mixer is made up of two horizontal rotors with protrusions placed in a casing. It is provided with a feed door and hopper at the top and a discharge door at the bottom. An early developed internal mixer is the Banbury mixer, an important and novel feature of which is a vertical ram to press the mass into contact with the two rotors. The basic design of the machine (Figure 2.4) includes two rotors that operate at a slight speed differential. The rotors are non-interlocking. Mixing or shearing action occurs between the rotors and the sides of the mixer, and between the rotors themselves. Pressure is exerted on the batch using a ram which closes the feed opening. Discharge of the batch occurs at the bottom of the mixing chamber (Figure 2.5). The rotor design is such that material in the chamber is constantly being displaced, corresponding to the crossblending action of the mill operator cutting the batch on a two-roll mill. The compound is subjected to the shearing action of the rotors against the sides, and the action of the rolling bank between the rotors.

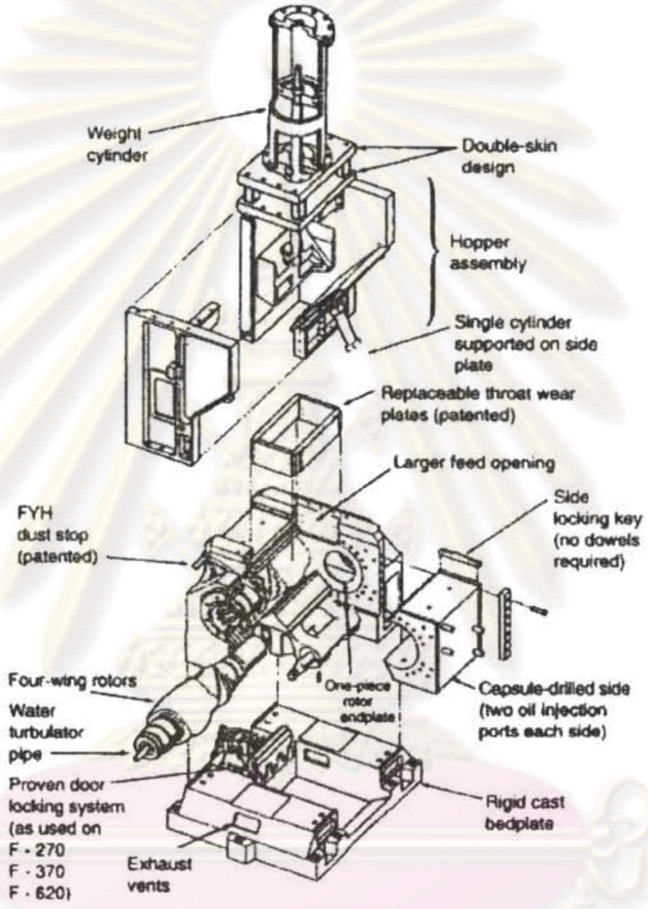


Figure 2.4 Basic banbury mixer [4].

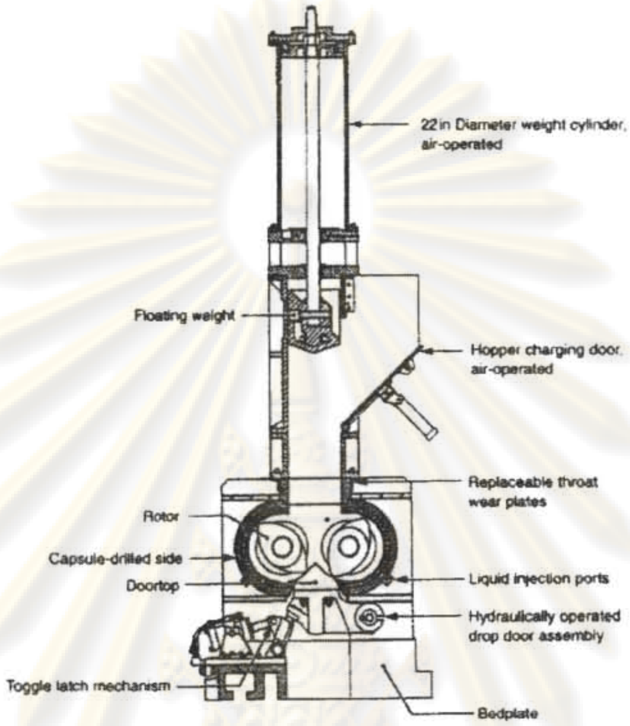


Figure 2.5 Banbury mixing chamber [4].

The selection of rotor speeds, mixer size and the extent of materials-handing automation are all related to the demands of the specific sector of the rubber industry. At one extreme there is the massive quantity of compound mixed by tire manufacturers, where most compounds are two-stage mixed (masterbatch and final) using high speed, automated materials-handing equipment, and large mixers. In many case their compounds are mixed in a single cycle to reduce handling and inventories.

The operation of internal mixers is power-intensive and a given job is performed at a much higher speed and over a much shorter time than on a two-roll open mill. However, the major vulcanizing agent such as sulphur is usually added later on a two-roll mill to eliminate scorching difficulties. Even if this is not practised, the mix is, of necessity, passed through a two-roll mill after being discharged from the internal mixer in order to convert it from irregular lump to a sheet form for convenience in subsequent processing.

The major advantages of the internal batch mixer are as follows:

1. Highly reproducible cycles
2. Minimum dependence upon operator skills
3. Large capacity and high output
4. Relatively short mixing cycles
5. Potentially clean factory operations

But there are some disadvantages, compared to mill mixing:

1. More rapid temperature rise in mixing
2. More time needed for cleaning equipment
3. Much higher initial investment

2.3.2 Two-roll mills

A two-roll lab mill (Figure 2.6) is a device for preparing for preparing small quantities of mixed compound. This mixing device is usually set for a ratio of roll surface fructional speed of about 1.25 : 1. The rubber tends to gather on the hot slow roll, i.e. the front roll in the form of a continuous band, the excess forming a 'bank' which churns around the nip. When the rubber has passed through the nip for the first time it may not, however, be conditioned to the state when it will adhere to the roll. Consequently, the operator must stretch under the roll, pull out an end and press it to the face of the front roll to help it up over the crown and back into the nip. This action may have to be repeated several times.

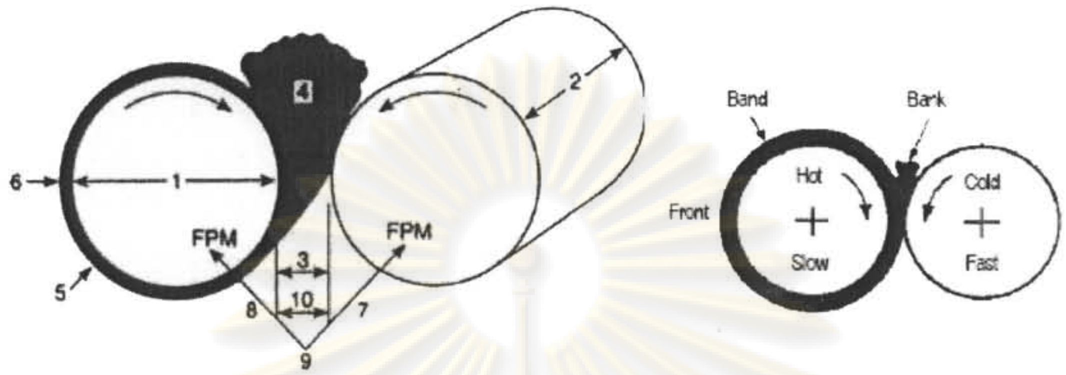


Figure 2.6 Two-roll mill [4].

1	Diameter (D)	Usually same for both rolls
2	Face length (L)	Roll length (mill sizes expressed as DxL)
3	Roll gap	Distance between rolls
4	Bank size	Material sitting above gap
5	Banded roll	Roll which material follows
6	Front roll	Roll on operator's side
7	Slow roll	Roll rotating at the slowest speed
8	Fast roll	Roll rotating at the fastest speed
9	Friction ratio	Roll speed ratio
10	Separating force	Resultant force exerted by material in roll gap

Powders are now added into the gap, with frequent pan sweeping to recover increments which drop through. Process oil or plasticizer is also added, usually after part of the filler content has been incorporated. The compound rubber was cut from one side of the mill to the other side but it should not be torn, to crossblend the batch. At the conclusion of mixing (usually determined by the judgment either of the operator or a supervisor) the batch is cut from the mill for cooling and storage.

A major advantage of mill mixing is the high shear developed at the mill nip; this breaks up agglomerates and drives incorporation of ingredients. Furthermore, the massive surface exposure imparts good cooling, thereby maintaining the stiffness of the compound. And due to the roll friction ratio, the rolling bank imparts further high shear.

The disadvantages of mill mixing usually far outnumber the advantages, they are:

1. Length of the mixing cycles
2. Dependence on operator skills
3. Dust and dirt levels that are typical
4. Difficulty in standardizing subjective procedures
5. Difficulty in controlling batch-to-batch uniformity

2.4 Sulphur vulcanization

The reaction between rubber (usually the diene rubbers-homopolymers or copolymers) and sulphur is very slow. Some inorganic metal oxides (Pb, Ca, Zn, Mg) were used to achieve sulphur vulcanization of NR at faster rates at high temperatures.

2.4.1 Accelerators

The sulphur vulcanization needs to incorporate small doses of one or more organic substances, known as accelerators. A variety of accelerators are currently available and they are more appropriately classified according to the speed of curing induced in their presence in NR systems. In the order of increasing speed of curing, they are classified as slow accelerator, medium accelerator, semi-ultra accelerator and ultra accelerator. The principal chemical types are guanidines, thiazoles, sulfenamides, dithiocarbamates, thiuram sulphides, xanthates, and aldehydeamines (Figure 2.7).

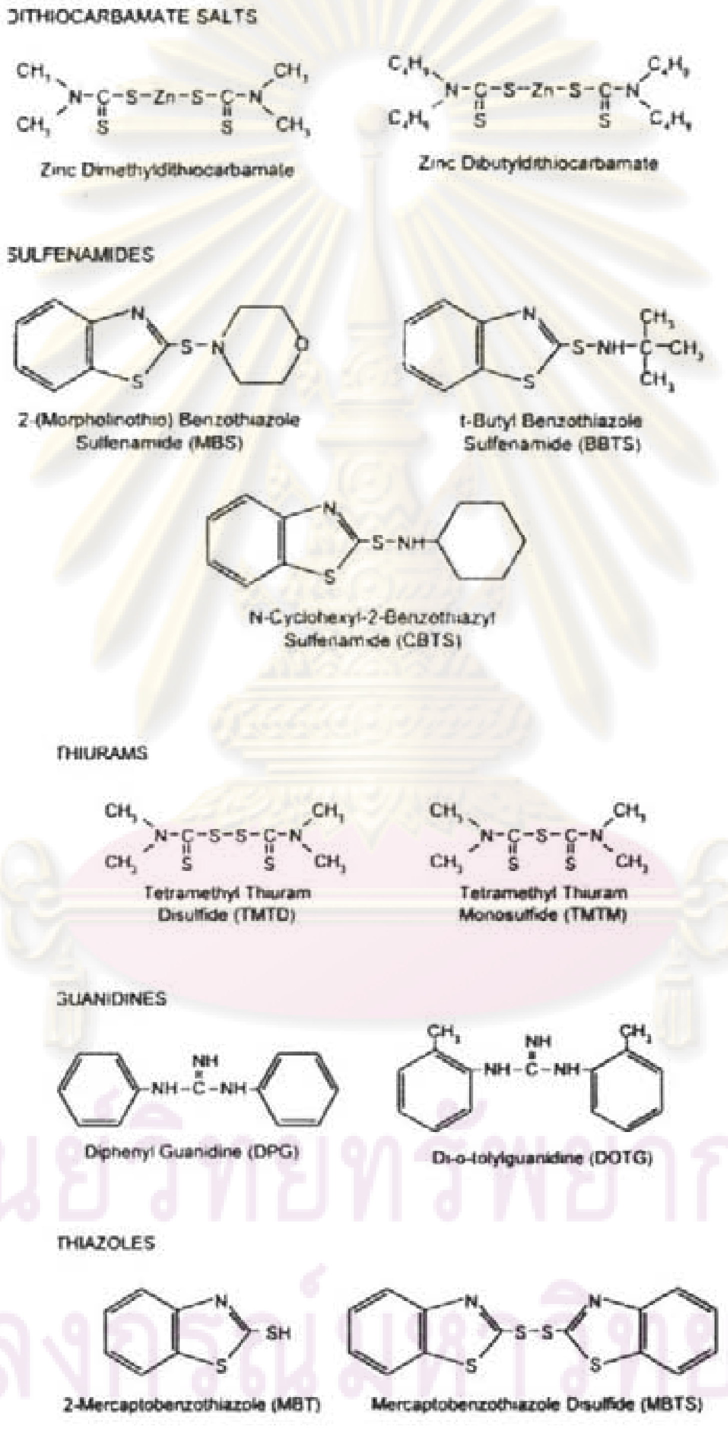


Figure 2.7 Accelerators for sulphur vulcanization of rubbers [5].

The accelerated sulphur vulcanization is associated with many advantages over non-accelerated vulcanization. Incorporation of about 0.2-2.0 parts of accelerator allows reduction of sulphur dose from 8-9 parts to 0.5-3 parts and effective curing is achieved in a time scale of a few minutes to nearly an hour depending on temperature (100-140°C) and type of the selected accelerator. The low sulphur requirement of the accelerated sulphur vulcanization technology has eliminated bloom (migration of unreacted sulphur to the surface of the vulcanizate) which was a common feature of the earlier non-accelerated technology. Other consequences of low sulphur dose in accelerated vulcanization are production of vulcanizates of greatly improved physical properties and good resistance to heat and aging.

With progress of vulcanization, the tensile strength and modulus for some systems increase very sharply up to a point, pass through a maximum and a slow decreasing trend. For some other systems, the initial sharp gain in the value of the tensile parameters is followed by a long plateau region, a very slow increasing trend (Figure 2.8). The phenomenon of decrease in the tensile parameters beyond the maximum point (Figure 2.8, curve 1), usually known as reversion, is commonly observed with NR or IR. Reversion is generally not observed with SBR. The nature of change characteristic of SBR as depicted in Figure 2.8, curve 2, is commonly described as "marching cure" [6].

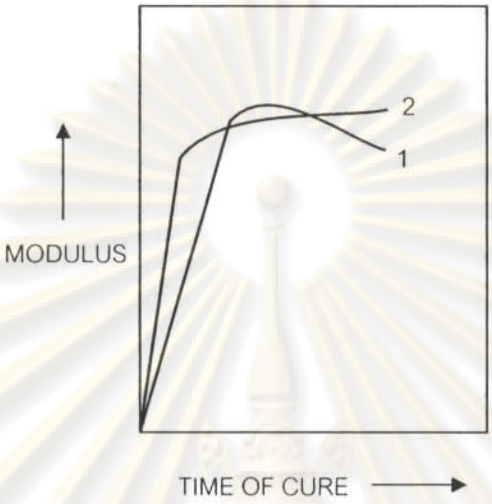


Figure 2.8 Plots of modulus vs time of cure showing reversion (Curve 1) and marching cure (Curve 2) [6].

A sharp drop in the physical properties such as tensile modulus for heating beyond optimum curing is undersirable; the plateau (or slow marching) effect is, however, desirable and advantageous in view of the fat that minor variations in time and temperature of vulcanization or extending the vulcanization process beyond the optimum curing time into the overcure zone would make practically no difference in or cause no deterioration of the physical properties.

Scorch or premature vulcanization during mixing or compounding and storage of the mix must be avoided. The scorch problem is very acute with ultra or fast accelerators. Rubber stocks are usually bad conductors of heat and therefore, flow of heat to the interior of a vulcanizing stock from outside is very slow. In thick items, the outer layers, through which the heat passes to the interior of the items, may reach a state of overcuring before the core or interior layers begin to cure. For such thick items, a slow accelerator with a prominent plateau effect is most suitable.

2.4.2 Activators [6]

The spectacular effects of modern organic accelerators in sulphur vulcanization of rubber are observed only in the presence of some other specific additives commonly known as activators. The activators are usually two-component systems comprising combinations of a metal oxide and a long chain fatty acid. A combination of zinc oxide and stearic acid is known to produce quite satisfactory results and is almost universally used. The primary requirement for satisfactory activation or promotion of accelerator action is good dispersibility or solubility of the activators in rubber. Oxides of some other bivalent metals such as, lead, calcium, magnesium, cadmium also act as activators in combination with stearic acid. The activators not only enhance the rate of curing, they also contribute to the development of desirable properties in the vulcanizates, The importance of the activator can be appreciated from the data given in Table 2.2.

Table 2.2 Effect of activator on vulcanization [6]

Time of Cure min	Tensile Strength, psi	
	ZnO in parts	
	0.0	5.0
15	100	2300
30	400	2900
60	1050	2900
90	1300	2900

Base compound: NR (pale crepe): 100; sulfur: 3; mercaptobenzthiazole (MBT): 0.5; temperature of vulcanization: 142°C.

2.5 Carbon black reinforcement in rubber [7]

Carbon black is produced by the incomplete combustion of petroleum products. Carbon black is a form of amorphous carbon that has an extremely high surface area to volume ratio. It is similar to soot but with a much higher surface area to volume ratio. Carbon black is often used as a pigment and reinforcement in rubber and plastic products. The most common use (70%) of carbon black is as a pigment and reinforcing phase in automobile tires. Carbon black also helps conduct heat away from the tread and belt area of the tire, reducing thermal damage and increasing tire life. Carbon black particles are also employed in some radar absorbent materials and in printer toner. The highest volume use of carbon black is as a reinforcing filler in rubber products, especially tires. While a pure gum vulcanizate of SBR has a tensile strength of no more than 2.5 MPa, and almost nonexistent abrasion resistance, compounding it with 50% of its weight of carbon black improves its tensile strength and wear resistance as shown below in Table 2.3.

Table 2.3 Types of carbon black used in tires [7]

Name	Abbrev.	ASTM desig.	Particle size nm	Tensile strength Mpa	Relative laboratory abrasion
Super abrasion furnace	saf	N110	20-25	25.2	1.35
Intermediate SAF	isaf	N220	24-33	23.1	1.25
High abrasion furnace	haf	N330	28-36	22.4	1.00
Easy processing channel	epc	N300	30-35	21.7	0.80
Fast extruding furnace	fef	N550	39-55	18.2	0.64
High modulus furnace	hmf	N683	49-73	16.1	0.56
Semi-reinforcing furnace	srf	N770	70-96	14.7	0.48

Practically all rubber products where tensile and abrasion wear properties are crucial use carbon black, so they are black in color. Where physical properties are important but colors other than black are desired, such as white tennis shoes, precipitated or fumed silica is a decent competitor to carbon black in reinforcing ability. Silica based fillers are also gaining market share in automotive tires because they provide better fuel efficiency due to a lower rolling loss compared to carbon black filled tires. Traditionally silica fillers had worse abrasion wear properties, but the technology has gradually improved to where they can match carbon black abrasion performance.

2.6 Literature Review

In 1980, Takaji, et al. [8] studied the process for preparing open-cell sponge rubber printing materials in which interconnecting passages among the cells are broad and valve-like pieces narrowing interconnecting passages. The weight ratio of the soluble starch to the water-soluble salt was in the range of from 1:9 to 1:3, mixed into 100 parts by weight of synthetic rubber (NBR). The cured product was separated from the mold and washed with water sufficiently to remove soluble starch and water-soluble salt. It adsorbed highly viscous pigment-containing ink having a viscosity of 2000 to 4000 cp (as measured at 25 ºC). The sponge rubber material can be used as a shock-absorbing material and clear prints.

In 1994, Uchida, et al. [9] produced the sponge rubber having uniform and fine open cells by kneading a specified rubber composition with a specified salt powder and a specified surfactant, then molding and vulcanizing the mixture. A rubber composition comprised a stock rubber (NBR) 100 parts by weight, 0.3 parts by weight of vulcanizing agent (S), kneaded together with $CaCO_3$ 550 parts by weight which has a particle diameter of 0.002-0.250. Dilute hydrochloric acid was used for the dissolution $CaCO_3$ removal. The sponge rubber was applied for shock absorbing material, filter media and ink pad.

In 1995, Kazumi et al. [10] studied a process for producing a sponge rubber stamp having open cell. The process comprised steps of superposing an unvulcanized rubber sheet (A) on rubber sheet (B). Rubber sheet A containing a water-easily soluble powder 400 parts by volume of sodium chloride having a particle diameter of 0.090 to 0.30 mm which were added to 100 parts by volume of rubber composition. Rubber sheet (B) containing an acid-soluble powder 260 parts by volume of calcium carbonate having a particle diameter of 0.053 to 0.105 mm which were added to 100 parts by volume of rubber composition. They were pressed to form an integral laminate at 150°C for 15 minutes. The integral laminate was treated with water to make the layer (A) porous. The surface of the layer (B) of the integral laminate was sculptured by a laser beam (carbodioxide gas laser having an intensive of 80-400 W and a spot size of 40-80 micrometre) to form a stamp surface thereon. No microcracks occured in the stamp at the formation of the stamp surface.

In 1996, Ishikawa et al. [11] studied the manufacture of a sponge rubber print body having open cell by vulcanizing a masterbatch in which rubber, water soluble fine sodium chloride of 80-100 mesh (0.149-0.176 mm), vulcanizer, filler and organic synthetic fiber staple having specific fiber length of 0.2 to 2 mm were kneaded. This masterbatch was vulcanized, then the powder is removed to obtain a sponge rubber having open cell. They found that the sponge rubber can be used to hold the pigment ink with viscosity of 500-2000 cps, the clear seal without a blot or a blur was able to be performed over the long period of time.

In 1997, Shigehiro et al. [12] prepared the porous rubber stamp material having the open cells which comprises a print layer and an ink-occluding layer. The print layer have a spring hardness of 30 to 40. Sodium chloride (600 parts by volume) having a particle diameter of 0.030-0.060 mm was added to NBR rubber composition a print layer (100 parts). Thickness of the compound print rubber layer was 1.5 mm. The ink-occluding layer have a spring hardness of 10-20, sodium chloride (700 parts) having a particle diameter of 0.090-0.30 mm was added to a synthetic rubber composition (100 parts). This sheet has a thickness of 3.5 mm. The print layer sheet was superposed upon the ink-occluding layer sheet. The vulcanization was carried out at 150°C under 150 kg/cm^2 for 15 minutes. Then, the material was washed with water to remove salt, and dried. The porous rubber stamp material can be used for the continuous sealing of a private seal, an address seal and a date seal.

In 2000, Kazumi et al. [13] studied a rubber stamp which can be used several times for stamping after being inked once. A rubber composition contained synthetic rubber (NBR) 100 phr , a vulcanizing agent 1 phr, a filler and sodium chloride 350 phr (a particle size of 0.03-0.06 mm). The unvulcanized rubber sheet with a thickness of 1.5 mm was produced, subsequently, it was compressed at 160°C under 50 kg/cm^2 for 15 minutes. The spring degrees of hardness of the sponge rubber layer is 15-35. A laser beam used is carbon dioxide laser having an intensive of 80-400 W and the spot has magnitude of 40-80 micrometers.

In 2002, Kyung-il et al. [14] studied acoustic properties changes of nitrile butadiene rubber (NBR, acrylonitrile content 33%) specimens with carbon black as filler and with different sulfur contents (1.0, 2.0, 3.0 phr). Rubber mixing was carried out by using an F-series Banbury mixer. The mixing procedure was divided into the two stages. The rubber mixes were vulcanized in a hydraulic press at 150°C. When carbon black filler was added, the acoustic property changes of NBR with increasing of sulfur content were small. The hardness was much changed because of the crosslinking density change in the specimen.

In 2004, Susmita et al. [15] studied preparation and properties of nanocomposites prepared with different grades of nitrile rubber with acrylonitrile content of 19, 34 and 50%, with Na-montmorillonite clay. The nanocomposites showed improved mechanical properties. The extent of the increase in strength, varying from 38 to 166%, was dependent on the nature of the base rubber and its polarity. When NBRs with different nitrile contents were compared, the improvement in the strength was found to be higher for NBR with a higher acrylonitrile content.

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Acrylonitrile butadiene rubber	Cosan (Thailnd) Co.,Ltd.
2. Di(2-ethylhexyl) phthalate (DOP) plasticizer	Cosan (Thailnd) Co.,Ltd.
3. Vulcanizing agent sulfur	Cosan (Thailnd) Co.,Ltd.
4. Accelerators	Cosan (Thailnd) Co.,Ltd.
- Thiazoles: MBTS (mercaptobenzothiazole disulfide)	
- Guanidines: DPG (diphenyl guanidine)	
5. Zinc oxide and stearic acid (activator)	Cosan (Thailnd) Co.,Ltd.
6. Ralox®LC (antioxidant)	Cosan (Thailand) Co.,Ltd.
7. Carbon blacks: N-220, N-330, N-774	Cosan (Thailand) Co.,Ltd.
8. Surfactants	Kao Industrial Co.,Ltd.
- Sodium lauryl ether sulfate (anionic surfactant)	
- Sodium alkyl benzene sulfonate (anionic surfactant)	
- Alkylene oxide derivative: Polyethylene glycol distearate (nonionic surfactant)	
9. Water-soluble salts	Union Chemical 1986
- Sodium chloride ($NaCl$)	
- Sodium nitrate ($NaNO_3$)	
10. Solvent	Union Chemical 1986
- Methanol	
- Water	
11. Pre ink stamp X-Stamper	Shachihata

3.2 Apparatus

Apparatus	Model, supplier
Grinding Machine	Waco#1
Brabender	Yi Tzung Precision Machinery, Taiwan
Two-rolls mill diameter 12 inches	Collin W100T, USA
Moving Die Rheometer MDR 2000	(Techpro, rheotech MD+)
Hot compression moulding	Hong Yow Thai, Thailand
Ultrasonic cleaner four transducers, 9 liters	(ACE Altimate)
Durometer type C	REX 2000
Scanning electron microscope	JEOL model:JSM-6301F and 5410
Desiccator	-
Oven	WTB Binder ED53

3.3 Sample preparation

3.3.1 Preparation of fine sodium salt powder

Sodium salts (NaCl and $NaNO_3$) were ground in a grinding machine, then passed through a wire mesh having sizes of 100, 300 and 400 mesh (diameter of 0.14, 0.045 and 0.034 mm, respectively). The salts were kept in a desiccator to prevent humidity and agglomeration of the fine powder.

3.3.2 The mixing of compound rubber

The NBR rubber was compounded with ingredients of vulcanization system. The temperature for rubber compounding was set at 95 °C. First, the rubber was charged into the Brabender chamber. Then, the activators (zinc active and stearic acid) and antioxidant (Ralox LC) were added at the same time. After that, fillers: carbon black, plasticizer (DOP) and surfactant were added. Fine powder salts (NaCl or $NaNO_3$) were added later. The mixture was finally added vulcanizing agent (sulfur) and accelerators (MBTS, DPG).

For the batches tested the effect of surfactant addition (in order to help the dissolution of sodium salt), the surfactant was also added 120 phr.

In this work, many parameters affecting on the properties of the sponge rubber produced were varied for the investigation, as follows:

- Three types of surfactant: anionic (Neopelex F-50 and Emal 270TH), nonionic (Emanon 3299R).
- Two types of carbon black : N220, N330 and N774.
- Various contents of carbon black: 20 and 50 phr.
- Various contents of salt: 600, 700, 800 and 1000 phr.

The total recipes of compound rubber are shown in Appendix A; Table A.3-A.4

Formula code in Appendix A.1-A.2 can be illustrated below;

20C-200 Number prefixed to C means amount of carbon (phr) filled onto the formula, C means carbon black, and 200 means type of carbon black; N-220

800Cl-100 Number prefixed to Cl means amount of NaCl, Cl means type of sodium chloride, 100 means size of sodium chloride (mesh), the smaller the sodium chloride size, the greater the value of the mesh.

$NaNO_3$- Cl is converted into form of NO3 for salt system, while on surfactant system, the designation is suffixed; for examples in Figure 3.1.

20C-200
800Cl-100
Neopelex

20C-200
800NO3-100
Neopelex

Figure 3.1 Codes of each recipe.

The addition of each composition was performed at each step of which profile of torque on mixer with the mixing time was demonstrated in Figure 3.2.

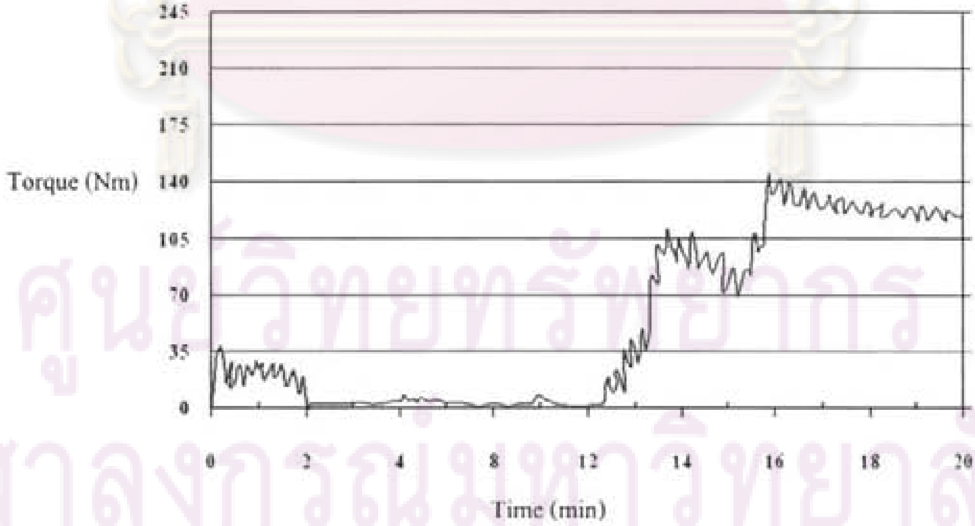


Figure 3.2 Profile of torque on mixer with the mixing time.

Ten steps of rubber compounding are as follows :

At 0 minute - the rubber was added
At 2nd minute - the activators and antioxidants were added
At 4th minute - the filler was added
At 8th minute - 1/5 of the mixture (plasticizer, surfactant and powder salt) was added
At 10th minute - 2/5 of the mixture was added
At 12th minute - 3/5 of the mixture was added
At 14th minute - 4/5 of the mixture was added
At 16th minute - the remaining mixture was added
At 18th minute - the vulcanizing agent and accelerator were added
At 20th minute - the compounded rubber was transfered to a two-rolls mill

3.3.3 Hot compression

In the first step it was preheated to temperature of 155°C for 15 minutes. Then, the compound rubber was placed in a mold. The mold is closed with a top force or plug member, pressure is applied to force the material into contact with all mold areas, heating was supplied and pressure was maintained until the molding material has cured. Time used in the compression process depends on the cure time of each compound rubber. There are two types of molds prepared in this work: character mold and smooth surface mold. The monolayer of sponge rubber provides both designed imprint and ink absorption capacity.

3.3.4 Removal of sodium salt

The vulcanized rubber without surfactant was washed with water at 60°C to remove the sodium salts for 3-15 h for NaCl and 3-5 h for $NaNO_3$.

For the vulcanized rubber containing the salt and the surfactant, the cure product was immersed in methanol for ½ hour, followed by ultrasonication in 60°C water for 3 h. The cured product was dried at 40°C in an oven.

3.4 Physical property tests

3.4.1 Hardness test (ASTM D2240)

The hardness property of the specimen was measured by type C Shore durometer (used for the soft sample). The specimen thickness was 6 mm minimum value. The indenter of durometer was pressed on sample surface for 3 seconds and read the hardness value.

3.4.2 Scanning electron microscope (SEM)

The specimen fracture surfaces was coated by gold viewed by SEM at x500 x200 and x50 magnifications.

3.5 Moving die rheometer test (MDR test)

The MDR test was used to determine the M_L- minimum torque, M_H- maximum torque, scorch time(ts_2) and cure time(tc_{90}). The temperature was set at 155°C. A cure curve by plotting the torque versus time.

The minimum torque, M_L shows the lowest elastic modulus or viscosity of the uncured compound of the rubber compound.

The maximum torque, M_H attained during specified period of time when plateau or maximum torque is obtained.

The scorch time was measured when the torque curve increased from minimum torque in two units (such as 2 dn.m).

The cure time (or vulcanization time) was measured when the torque curve increased from the minimum torque in 90 percent of the difference between maximum torque and minimum torque.

3.6 Adsorption of ink

3.6.1 Adsorption of oil ink

The sponge rubber prepared above was added X-stamper oil ink by dropping the ink all over the surface of the sponge rubber at the rate of 1 drop/min. The adsorbed ink weight was determined at one hour after the ink dropping.

In addition, in this work, the time required for the inking until the sponge rubber was fully filled with ink was monitored. This time is counted from the start of dropping ink until the first ooze out of the rubber was observed on paper.

After the sponge rubber were fully filled with oil ink, it was assembled in the pre-ink stamp case.

3.6.2 Impression test

The impression test was performed by oozing out the ink on a paper with lightly press 300 times per 2 minutes. The quantity of imprints was checked and number of clear impressions before re-inking was recorded. Clear prints was observed while continuing the printing or stamping operation for a long time. The quality of print was compared with pre-ink rubber stamp in the market.

3.7 Compound cost

Cost of the rubber compound sample was calculated on the basis of 10.5 g weight per piece. The costs of rubber compounds are shown in Table 3.1.

Table 3.1 Calculated cost of raw material sponge rubber

MATERIAL'S NAME	COST PER UNIT	Weight (g)	%By Weight	%UNIT COST
NBR RUBBER	105	40.8	8.91	9.36
Sulfur	12	0.61	0.13	0.02
ZnO	68	2.04	0.45	0.30
DOP	51	12.24	2.67	1.36
Stearic acid	25	0.82	0.18	0.04
DPG	185	0.12	0.03	0.05
CARBON BLACK	32	24.48	5.35	1.71
RALOX LC	185	0.82	0.18	0.33
MBTS	125	0.41	0.09	0.11
$NaNO_3$	50	326.37	71.31	35.66
NaCl	8	0.00	0.00	0.00
Neopelex	56	48.96	10.70	5.99
TOTAL		457.67	100.00	54.94
Weight/a square meter	6.80			
COST =	**54.94**	Baht/kg.		
	373.58	Baht/ M^2		
Weight of rubber+ waste 10%	10.50	gram/piece		
Cost of rubber+ waste 10%	**0.58**	Baht/piece		

The cost of surfactant are used in this research have following:

Cost of Neopelex F-50 = 56 Baht per kilogram

Cost of Emal 270TH = 50 Baht per kilogram

Cost of Emanon 3229R = 62 Baht per kilogram

CHAPTER IV

RESULTS AND DISCUSSIONS

In this work sponge rubbers were prepared. The porosity resulted from open cells inside the rubber vulcanizates was produced by salt leaching. Different types of salt (NaCl and $NaNO_3$), sizes (100 and 300 mesh) and contents (800, 600 and 1000 phr) of salts were investigated to see effect on the sponge rubbers' properties. In addition, effect of different types of carbon black (N-330 and N-220) and contents of carbon black (20 and 50 phr) on the properties of sponge rubber were also studied.

For the sponge rubbers prepared using $NaNO_3$, both types of the carbon black were used because of their highly demanded reinforcement. The content used is 20 phr because the salt removal from the rubber is easy. On the other hand, the sponge rubbers prepared using NaCl, the mixed surfactant helps increasing the capacity in rubber removal salt, so 60 phr carbon black type 774 was used because of it helped to increase strength and hardness of rubber vulcanizates, gave the best press character surface.

In order to increase efficiency of salt leaching from the rubber sample the use of surfactant is also implemented. Two types of surfactant chosen for the study were anionic (Neopelex F-50 and Emal 270TH) and nonionic surfactant (Emanon 3299R).

For the actual application, the sponge rubber is contained in a holder to use as an imprint. Thus, two different components of imprint were set to find the imprint composition which provides the designed imprint quality. The ink adsorption and imprint quality of the mono-layer sponge rubber from this study were compared with the commercial double-layer rubber. The double-layer rubber, an upper layer was produced using larger salt particle for ink absorption quality, and a lower layer, was produced using smaller salt particle for clear imprint quality.

The properties of all rubber samples determined are as follows: cure characteristic, removal time of sodium salt, physical property, ink adsorption, and impression test. To be useful in commercial production, the time required for sodium removal must be minimized. In addition, the rubber product should provide high imprint quality on paper.

4.1 Preparation of sponge rubber from NaCl and NaCl-surfactant

For sponge rubber of which the open cell was produced from salt leaching using NaCl, removal weight of sodium salt was determined.

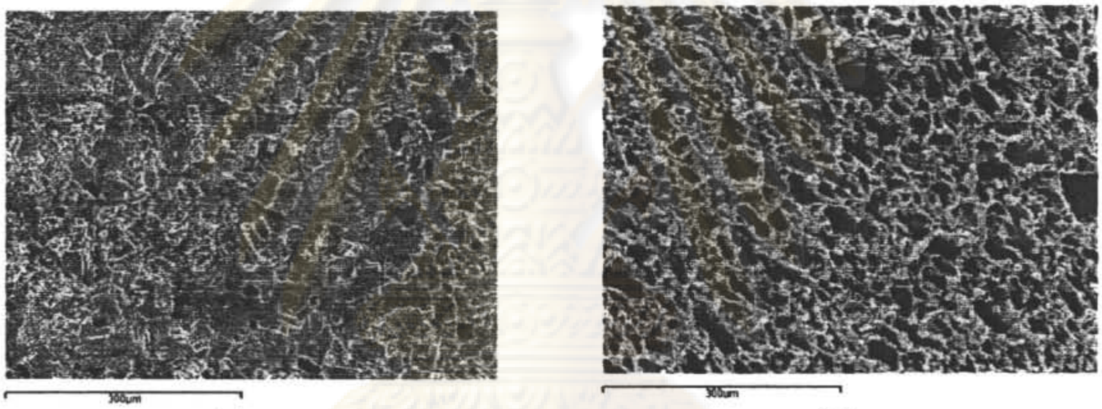
Removal weight of sodium salt

Sodium salt was washed out from the rubber vulcanizates in the ultrasonic bath at 60 °C for 3, 10 and 15 hours. The leached vulcanizates were then dried at 40 °C in an oven. The effects of salt content and their particle size, carbon black type and content of salt removal from the rubber were determined.

Removal weight of sodium salt represents content of sodium chloride exuded out of the rubber. High value of removal weight corresponds to amount of salt washed out from the rubber vulcanizate and open cells inside the rubber.

Scanning electron microscope (SEM)

The pore size and pore distribution in NBR sponge rubbers were identified as dark area in the SEM micrograph at x200. A lot of pore distribution represents amount of open cell in rubber. Figure 4.1 (a) shows close cells inside the rubber vulcanizate, so it cannot form sponge rubber. On the other hand, Figure 4.1 (b) shows the open cell inside the sponge rubber by salt leaching method. Amount of dark area shows potential of forming sponge rubber of each compound rubber formula.



(a) (b)

Figure 4.1 SEM micrographs of the fracture of salt filled NBR vulcanizates after removal of salts(200x magnification).
non sponge rubber (a) and sponge rubber(b)

Cure characteristic

Cure characteristic is used for determination of rubber compound property by using Moving Die Rheometer. The minimum (M_L) and maximum torque (M_H) value of the rubber compound were obtained. These two parameters were used to determine the scorch time in rubber curing process. The minimum torque shows the lowest elastic modulus or viscosity of the uncured compound of the rubber compound, whereas the maximum torque defined as the highest torque obtained during a specific period of time, and can be related to vulcanizate's modulus and hardness. Moreover, the curing time is also measured. Normally, low curing time is useful for industrial application.

The first formula of sponge rubber was formula 1 (1000 phr NaCl), as shown in Table A.3. The formula 1 was the rubber vulcanizates prepared using NaCl, it was partly referenced by Takaji Funahashi. Rubber compound filled with salt at ratio 1000 phr salt (based on 100 part of rubber). The formula 1 was unable to be mixed because of its high shear stress inside the chamber of banbury mixer, so the rotor is unable to rotate. Therefore in this work, formula 2 was compounded, the amount of salt decreases to 800 phr. The result of salt leaching was detected. From SEM micrograph shows in Figure 4.2, it was found that salt was not removed out of the rubber completely. The rubber cannot form opened cell interconnection. The other properties of sponge rubber from rubber compound formula 2 are shown in Appendix B.

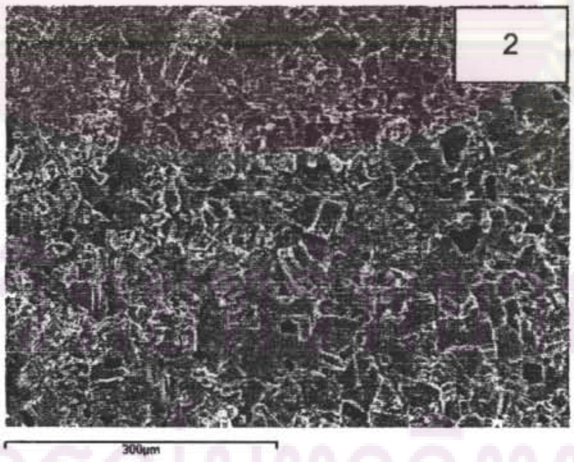


Figure 4.2 SEM micrographs of the fracture of formula 2 after removal of salts (200x magnification).

Thus, the formulation was then adjusted by adding carbon black type N220 and lowering amount of fillers, as shown in Figure 4.3. In order to increase open cell by salt leaching method, so it is suitable to make pre-ink stamp rubber product.

- Formula 2 and 3 were compared to present effect of carbon black type (N-330 and N220)
- Formula 3 and 4 were compared to present effect of carbon black content (50 and 20 phr)
- Formula 4 and 5 were compared to present effect of NaCl content (800 and 600 phr)
- Formula 4 and 6 were compared to present effect of particle size of NaCl (300 and 100 mesh)

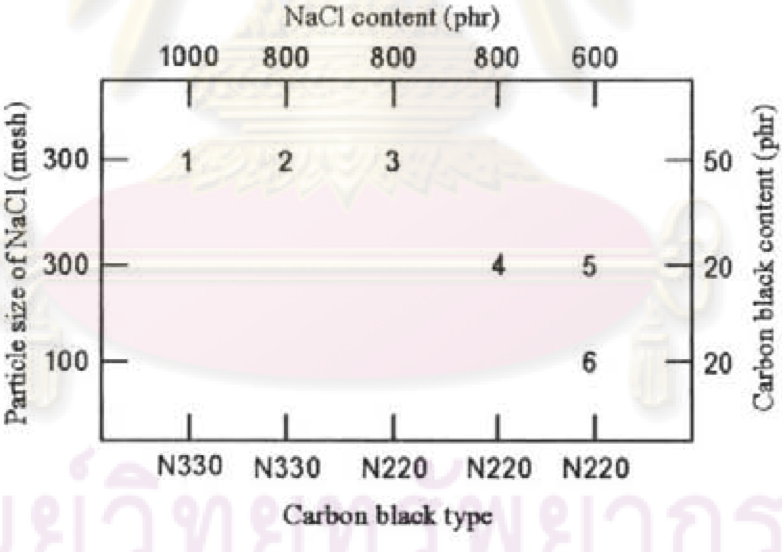


Figure 4.3 Formulation of NaCl-rubber vulcanizates.

The formulation of NaCl mixed surfactant, was shown in Figure 4.4 (formula 7 to 11). The 120 phr surfactant was added to improve efficiency of salt leaching, the suitable amount of NaCl and type of surfactant was verified to get the optimized open cell sponge rubber for pre-ink stamp.

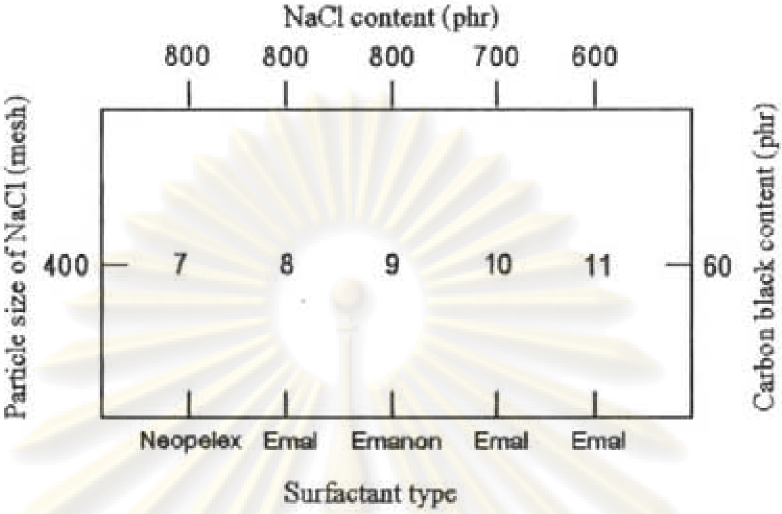


Figure 4.4 Formulation of NaCl mixed surfactant in rubber vulcanizates.

4.1.1 Effect of carbon black type and content on property of sponge rubber

Effect of carbon black type

The rubber formula 3 is compounded by using carbon black type N-220 instead of type N-330 in formula 2 because small size carbon black can allow the salt removal from the rubber more easily. Salt removal (%wt) and SEM micrograph were shown in Figures 4.5-4.6. It can be seen that the carbon black type has no effect on the removal of salts.

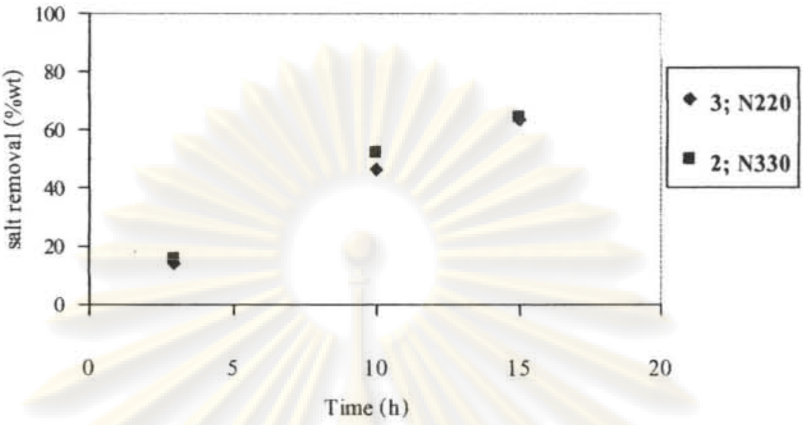


Figure 4.5 Effect of carbon black types on the salt removal of NaCl-rubber vulcanizate.

Figure 4.6 shows the morphology of the salt leaching vulcanizates. The pore size and pore distribution in NBR sponge rubbers could be identified as dark area in the SEM micrograph. After salt had been removed, black spots were observed in the rubber. The carbon black types have affected the fine open cell. The morphology indicated that in the sample with carbon black type N-220, salt can be removed more easily. As it can be seen that the black spots amount of formula 3 was higher than formula 2.

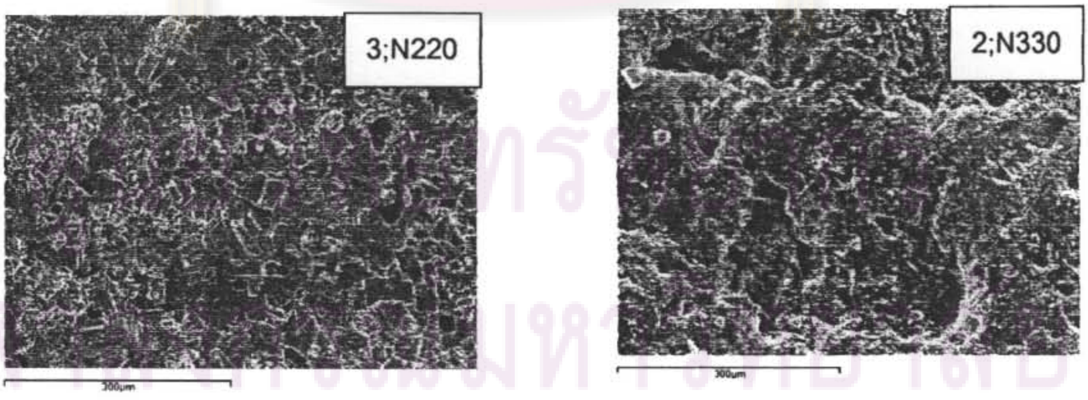


Figure 4.6 SEM micrographs of the fracture of NaCl rubber vulcanizate at various carbon black types after removal of salts (200x magnification).

Effect of carbon black type on the minimum torque, M_L and maximum torque, M_H are shown in Figure 4.7. The compound property of formula 2 and 3 is compared.

Figure 4.7 shows the minimum torque, M_L of the samples containing different types of carbon black at the same blend ratio. It was shown that the minimum torque, M_L of filled carbon black type N-220 compound rubber was higher than that of N-330 filled blend because of the higher surface area (N-220 has the smaller particle size). For rubber-grade carbon blacks, whose surfaces exhibit little porosity, the total area of the interface depends on both filler loading and the specific surface area of the filler. Due to the interaction between rubber and filler, the polymer molecules can be adsorbed onto the filler surface either chemically or physically. This adsorption leads to two phenomena, the formation of bound rubber and a rubber shell on the carbon black surface. Both are related to the restriction of the segmental movement of polymer molecules [7].

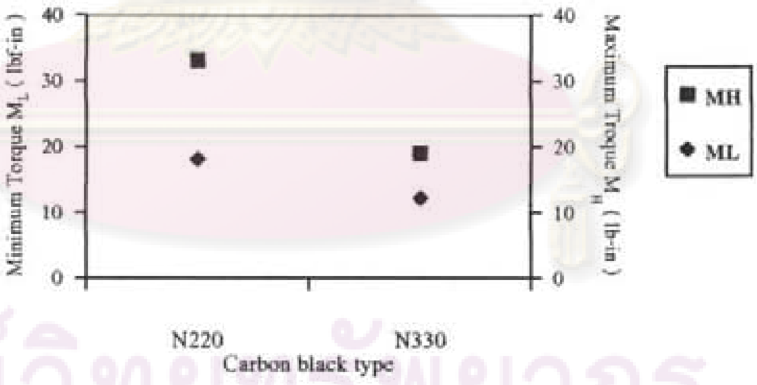


Figure 4.7 Minimum torque, M_L and maximum torque, M_H of NaCl-rubber compound at different carbon black type.

Effect of carbon black content

From the above result test of formula 3, it is found that NaCl was not removed from the rubber completely. So, next, the formula 4 is compounded as demonstrated in Table A.3. By reducing carbon black content from 50 phr to be 20 phr interaction force between particle size of carbon black with rubber molecule was decreased.

A schematic representation of the interaction between the nitrile rubbers and carbon black is shown in Figure 4.8.

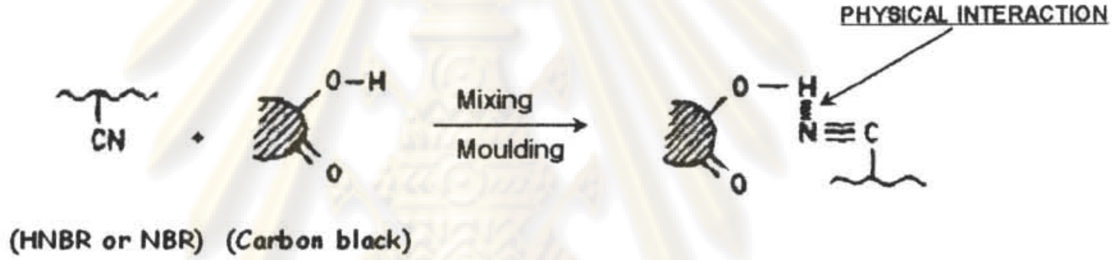


Figure 4.8 Bonding in HNBR or NBR with carbon black [16].

Formulas 3 and 4 are compared, as shown in Figures 4.9-4.10. For the effect of carbon black contents on salt removal, in Figure 4.9, the rubber vulcanizate having 20 phr carbon black gave higher salt removal than the sample with 50 phr carbon black. This can be explained by the interaction between NBR and the carbon black surface, probably the hydrogen bonding or Van der Waal's forces. The extent of interaction increases when the oxygen content on the filler surface increases [17]. The more adhesion between the carbon blacks and the NBR results in the difficulty of removing sodium salt.

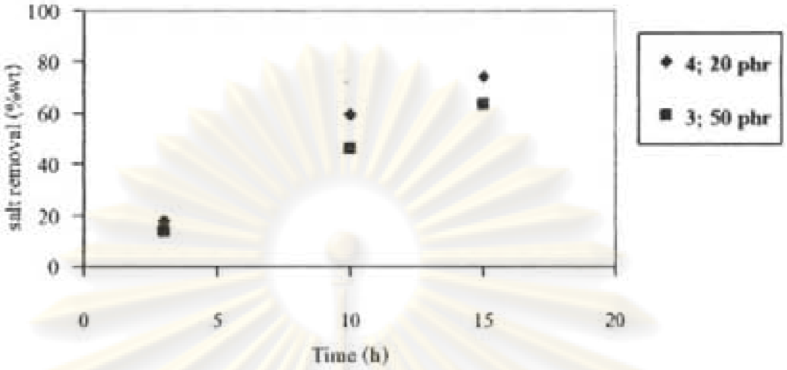


Figure 4.9 Effect of carbon black content on the NaCl removal from rubber composite containing NaCl (300 mesh, 800 phr).

For the effect of carbon black content, from SEM micrograph, it was found that more open cells were formed when carbon black content was low. [Figure 4.10]

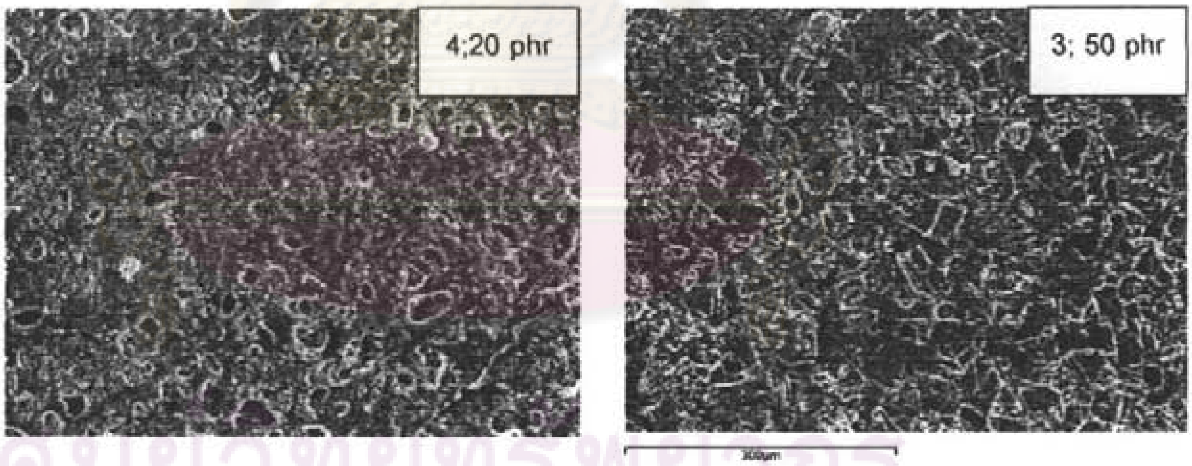


Figure 4.10 SEM micrographs of the fracture of NaCl filled NBR leached vulcanizates at various carbon black content (200x magnification).

Effect of carbon black content on rubber compound property is compared between formula 3 and 4 as shown in Figure 4.11.

When the N-220 filled blends with various carbon black contents were compared, it was found that the minimum torque, M_L and maximum torque, M_H of carbon black content of 50 phr was the highest, as shown in Figure 4.11.

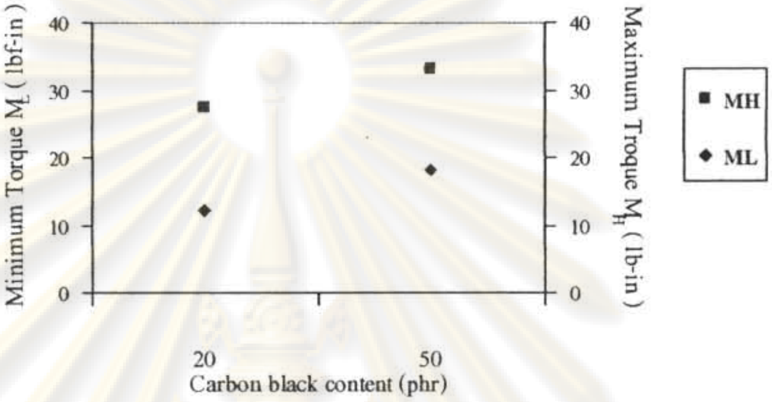


Figure 4.11 Minimum torque, M_L and maximum torque, M_H of NaCl-rubber compound at different carbon content.

Formula 4 containing 20 phr carbon black and carbon black type N-220 can be leached out salt from rubber. However there is still some NaCl salt inside rubber. This needs to be improved. So formula 5 is improved in order to increase salt leached out of the rubber, demonstrated in Table A.3.

4.1.2 Effect of NaCl content on property of sponge rubber

The salt content in the compound was reduced to 600 phr (800 phr for base case) in formula 5 for studied salt removal (%wt). Effect of NaCl content on rubber compound property compared between formula 4 and 5 as shown in Figures 4.12-4.13.

The minimum torque (M_L) and maximum torque (M_H) of NaCl at 800 phr of salts was higher than that at 600 phr because NaCl 800 phr gave the highest viscosity. Maximum torque, M_H value is generally used to identify the sturdiness of the compound rubber over crosslink. The higher the maximum torque value shows the stronger and higher crosslink density of the rubber.

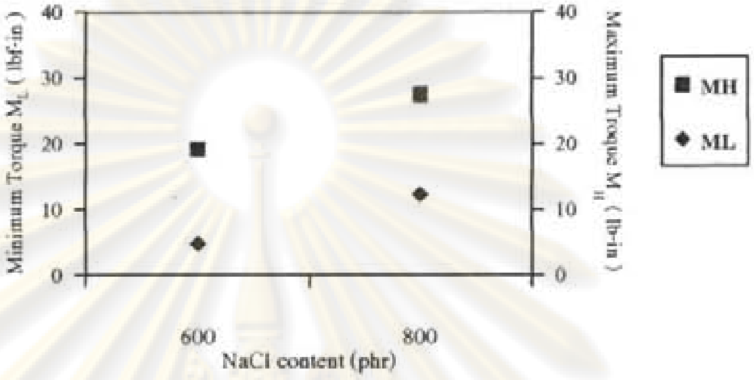


Figure 4.12 Minimum torque, M_L and maximum torque, M_H of NaCl-rubber compound at different salt content.

The scorch time is generally defined as the time for the onset of vulcanization at a particular temperature and thus represents the time available for processing. Cure time is the time required in the vulcanization step for the required amount of crosslinking to occur, yielding the desired level of properties. [18]

The scorch times (ts_2) and cure time (tc_{90}) [Figure 4.13] of NaCl filled compounds were affected by the content of salts. Among all the tested compositions, the scorch time was the highest for the sample salt content of 600 phr (fixed at 300 mesh). It can be explained that the higher surface area of salts and salts content make the system more viscous, therefore scorch time and cure time were shorten.

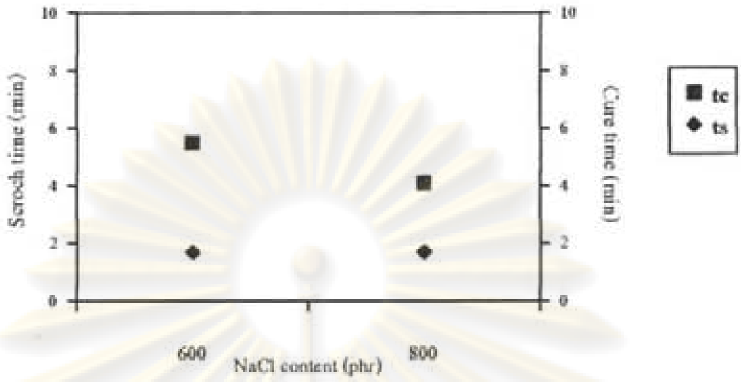


Figure 4.13 Effect of NaCl contents on scorch times and cure time of NBR compounds.

Minimum torque (M_L) of formula 5 was 4.8 dn.m, scorch times (ts_2) was 1.7 min. It was found that produces high quality compound rubber that precludes the complete running of compound rubber into the mould with complex characters [Figure 4.12 and 4.13] However, salt was not removed from the rubber completely [Figure 4.14]

The results of salt removal and SEM micrographs after salt removal are showed in Figures 4.14-4.15. Comparison results of NaCl content between formula 4 and 5 are also presented in these two figures. In Figure 4.14, for the effect of amount of sodium salts, it was found that % removal weight of sodium salt amount of 800 phr was higher than of 600 phr. The increase in content of sodium salts result in more interconnection between the salt particles making sodium salt dissolved more completely.

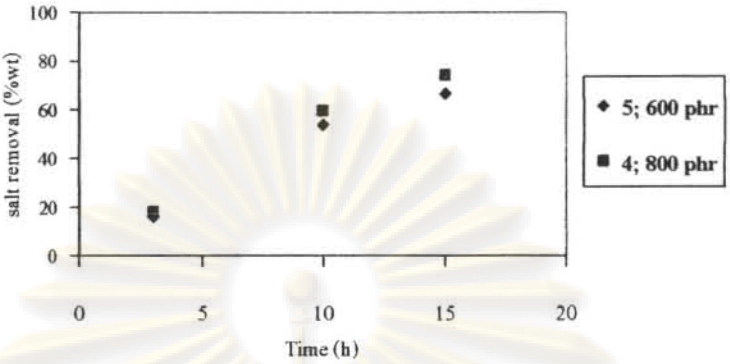


Figure 4.14 Effect of NaCl content on salt removal (%wt) of character surface rubber were washed out in the ultrasonic bath for 3 h, 10h and 15 h and then dried.

In Figure 4.15 for the samples of different salt content of 600 phr and 800 phr, the SEM micrographs show the sample filled with NaCl 600 phr has more rubber constituent than that of 800 phr. After removal of salt, the number of open cells of the sponge rubber filled with 600 phr of salt was lower than the other. From the results of removal salt and SEM morphology, the 800 phr NaCl was selected.

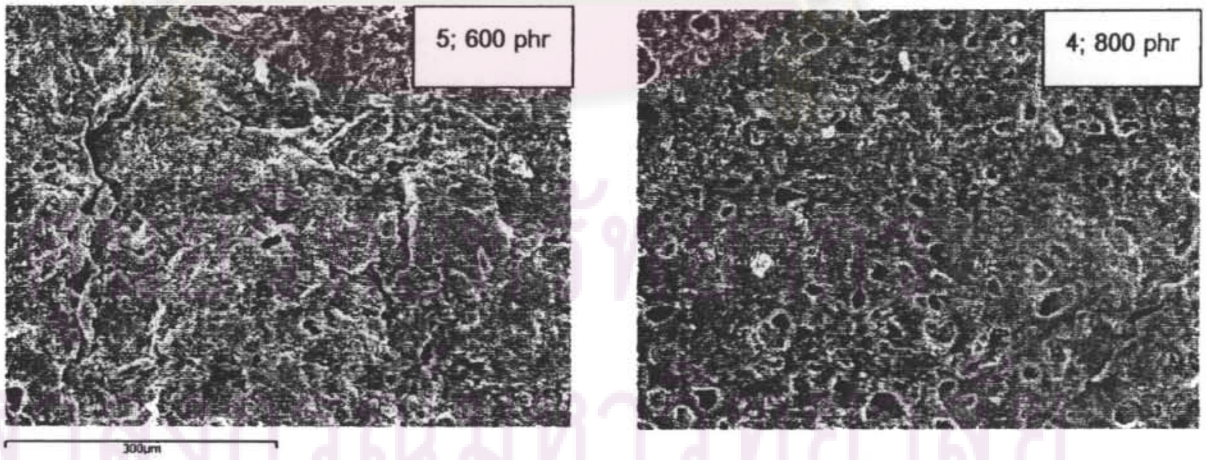


Figure 4.15 SEM micrographs of the fracture of NaCl filled NBR leached vulcanizates at various contents of salt (200x magnification).

4.1.3 Effect of particle size of NaCl on property of sponge rubber

According to the formula 1-5, the opened cell form texture could not be formed. Thus, the Formula 6 is developed and was showed in Appendix A (table A.3). In this formula, the NaCl size was increased from 300 mesh (0.045 mm) to be 100 mesh (0.140 mm). It was found that, the interconnection between the salt particles was also increased when the size of salt was increased.

Figures 4.16-4.17 showed the results of removal salt and SEM micrographs after removal salt of formula 4 and formula 6. It has to note that, the NaCl size of these two formulas was difference. In Figure 4.16, for the effect of particle size of sodium salts, it was found that salt removal (%wt) of sodium salt with 100 mesh in size was higher than that with 300 mesh. The increase in size of sodium salts result in more interconnection between the salt particles.

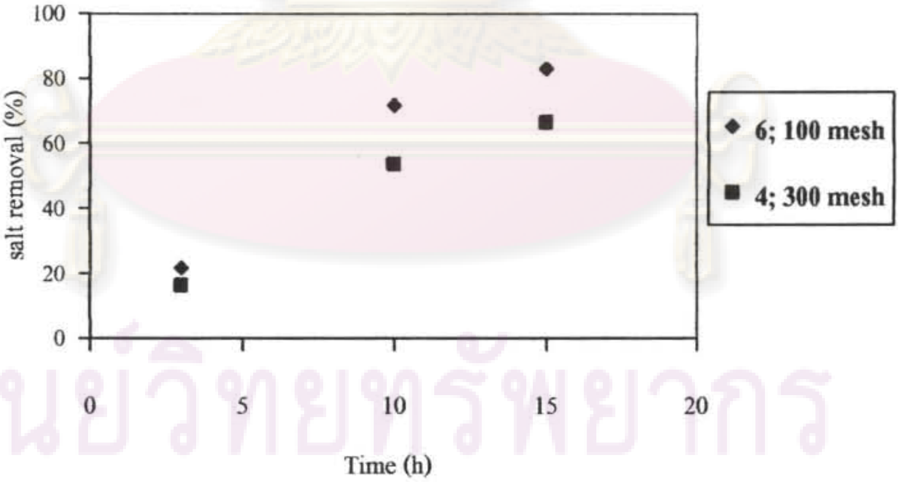


Figure 4.16 Effect of NaCl particle sizes on the salt removal of NaCl from the character surface rubber that was washed in the ultrasonic cleaner.

The particle size of salt were compared in the Figure 4.17 It was found that after removal of salt, the content of open cell of 100 mesh sample was higher than that of 300 mesh. The larger amount of salt can produce larger interaction between the salt particles than smaller ones, resulting in higher opened cell interconnection that water can permeate into the solid rubber easily.

The result shows that increasing NaCl size open cell cannot be formed completely. However, formula 6 provided a lot of open cells by using 20 phr carbon black type N-220 and 800 phr NaCl and NaCl 100 mesh.

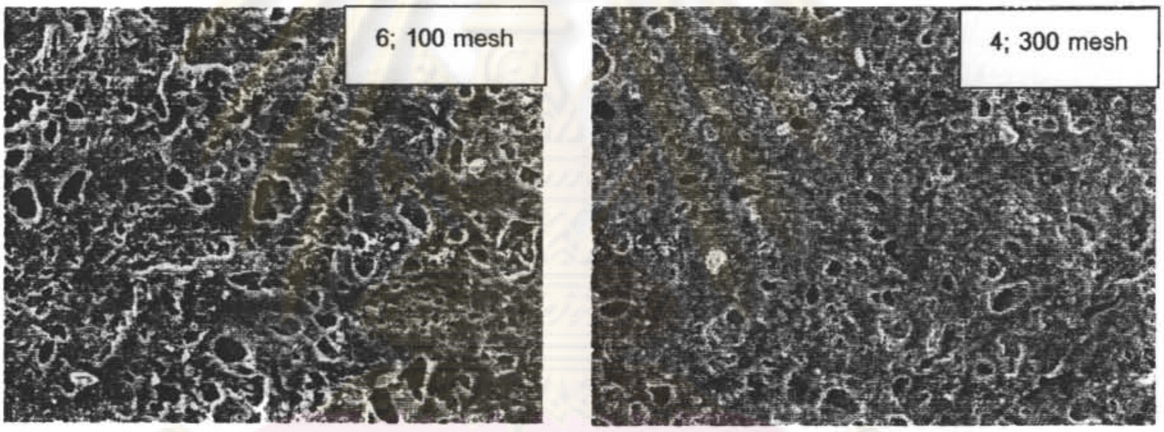


Figure 4.17 SEM micrographs of the fracture of NaCl filled NBR leached vulcanizates at various particle size (200x magnification).

Sodium salt, 100 mesh and 300 mesh, were mixed into the rubber then characterized the morphology by SEM micrograph. The particle sizes of salt in compound rubber were determined to recheck with particle size of salt passed wire mesh filtering (100 and 300 mesh).

From the SEM 500x magnification of salt-mixed rubber sample in Figure 4.18 (a) and (b); the size of NaCl 100 mesh was 50 micrometer while the sample 300 mesh was 20 micrometer in diameters. Regarding to the SEM-based scale calculation on size of the salt mixed in the rubber, the size of salt is inconsistent with the size of wire mesh filtering the salt because no air aspirator is placed on the salt grinder producing the applicable salt size pushed into grinding. Consequently, the grinded salt size becomes 50 microns; smaller than normal size, which the desired normal size is 140 microns.

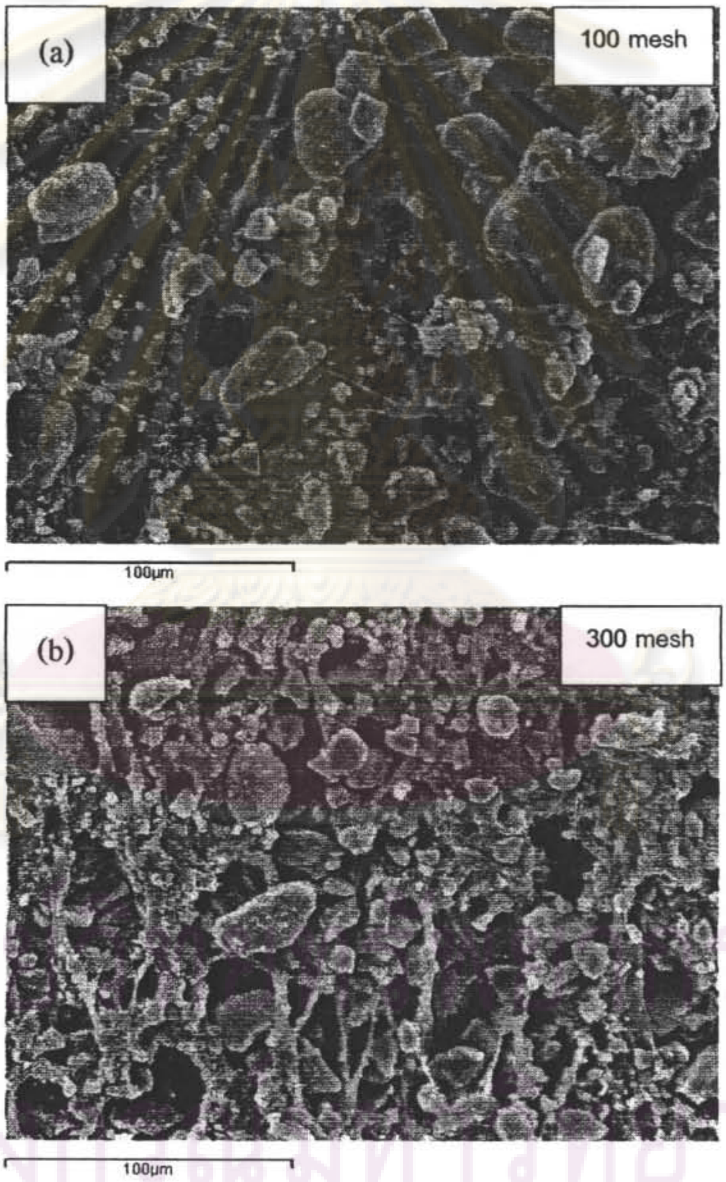


Figure 4.18 SEM micrographs of the fracture of NaCl filled NBR: (a) 100 mesh, (b) 300 mesh (500x magnification).

Effect of particle size of NaCl on property of compound rubber is compared between formula 4 and 6, shown in Figures 4.19-4.20. From Figure 4.19, the maximum torque in the rheograph is a measurement of cross-link density in the rubber but in this case the torque of NaCl and $NaNO_3$ filled compounds has affected more than cross-link of sulfur in the rubber. The maximum torque (M_H) of the sample containing 100 mesh (0.144 mm) was the highest.

The minimum torque (M_L) of NaCl at 100 mesh (0.144 mm) of salts was the highest, as shown in Figure 4.19. High minimum torque, M_L produces low quality compound rubber that precludes the complete running of latex into the mould with complex alphabets.

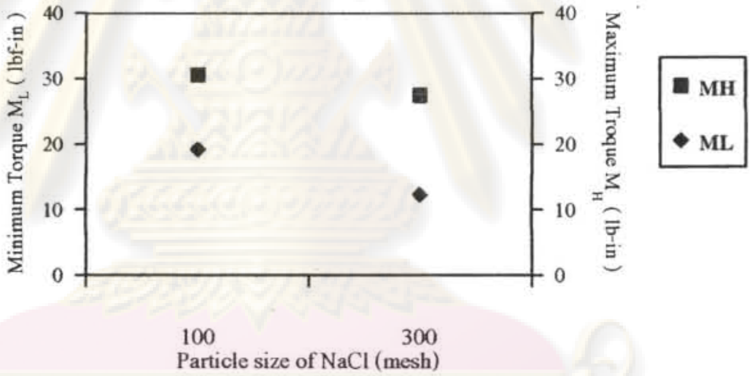


Figure 4.19 Minimum torque, M_L and maximum torque, M_H of NaCl-rubber compound at different salt particle size.

The scorch times (ts_2) and cure time (tc_{90}) [Figure 4.20] of NaCl filled compounds were affected by the particle size of salts. Among all the tested compositions, the scorch time was the highest for the sample with particle size of 100 mesh (fixed at 800 phr). It can be explained that the same result effect of salt content is obtained.

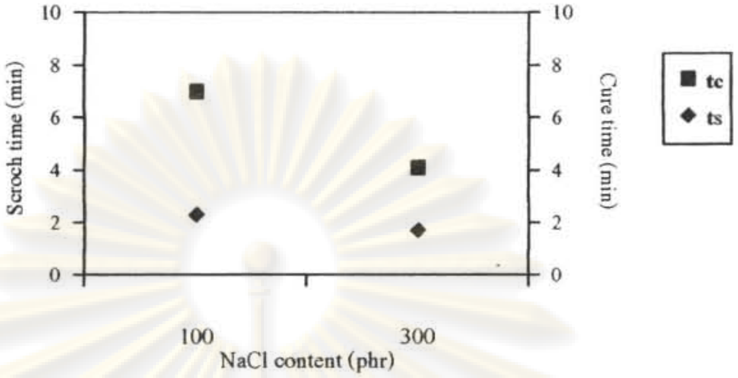


Figure 4.20 Effect of NaCl particle size on cure times of NBR compounds.

In this work, in order to enhance the washing out of salt from the rubber samples, surfactant was also added. Three types of surfactant (anionic: Emal 270TH, Neopelex F-50, and nonionic: Emanon 3299R) were chosen for the study.

4.1.4 Effect of surfactant type on property of sponge rubber

The formula 7, 8 and 9 were developed by adding different surfactant into rubber compound, as shown in Table D.1. To compare the efficiency of salt leaching, three surfactants were tested using the same recipe. Each was compounded by using NaCl 400 mesh, carbon black type N-774 with 60 phr carbon black, 120 phr surfactant and 1.5 phr sulfur curing. NaCl-mixed surfactant system increases the capacity in rubber removal, 60 phr carbon black type 774 was practical to strengthen the rubber press.

Effect of surfactant type on rubber compound property is compared between formula 7, 8 and 9, shown in Figures 4.21-4.22. From Figure 4.21, at the same blending ratio, the minimum and maximum torques (M_L and M_H) of the rubber blends containing Emal 270TH were the highest because of its highest viscosity.

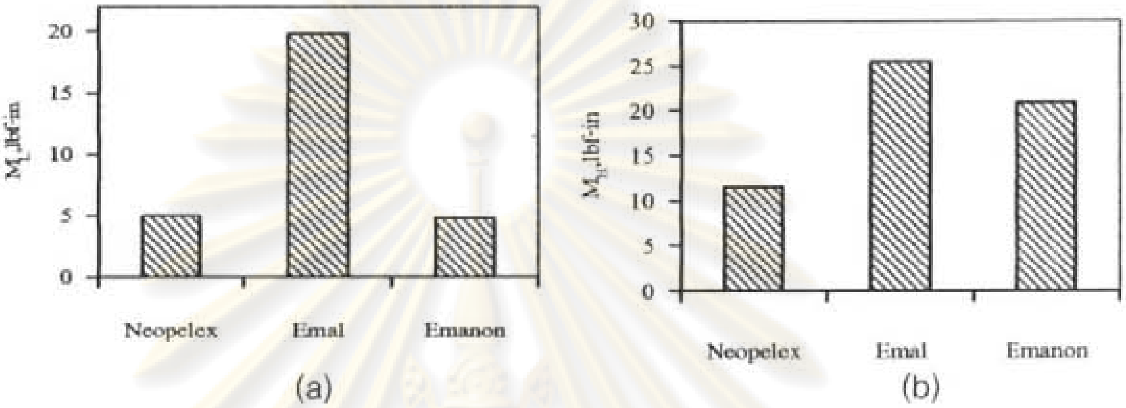
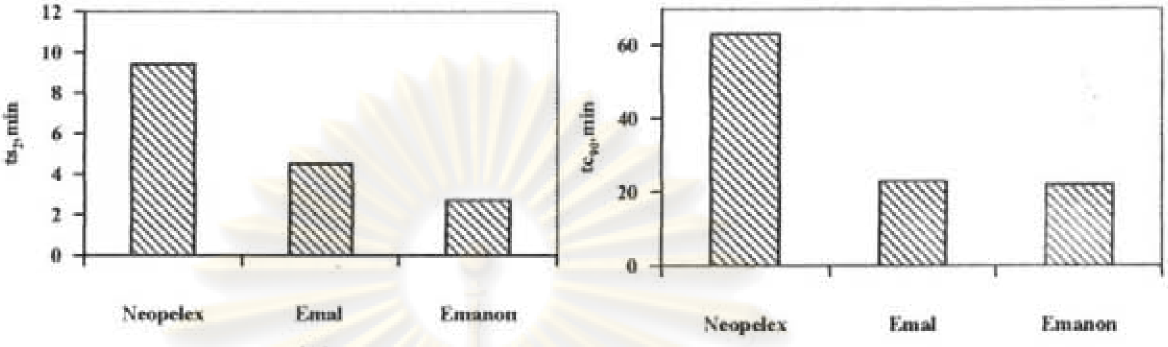


Figure 4.21 Effect of surfactant type on minimum (a) and maximum torque (b).

In Figure 4.22 the scorch time (ts_2) and cure time (tc_{90}) of the sample filled with surfactant Neopelex F-50 were higher than those of Emal 270TH and Emanon 3299R. It can be explained that the Neopelex F-50 has less % active ingredient than Emal 270TH and Emanon 3299R. It has 50% active ingredient of sodium dodecyl benzene. As the viscosity of the rubber blend was lower, the scorch time and cure time were higher. Scorch times value represents a nearly ceasing time of flow. This process is called "safety margin" to extrude the shape. If scorch time is short, the risk for broken products in the extrusion process is greater, and the rubber is likely to harden prior to being completely filled into the mould. Lesser cure time benefits the production; lesser time in compression increased the greater capacity in production. Emanon had cure time and scorch time suitable to produce pre ink stamp.

From cure characteristic of compound rubber, it was found that the formula suitable to produce sponge rubber was formula 8; Emal and formula 9; Emanon.



(a) (b)

Figure 4.22 Effect of surfactant type on scorch time (a) and cure time (b).

Surfactant types are compared between formulas 7, 8 and 9, as shown from the result of removal salt in Figure 4.23. As shown in Figure 4.23, the different types of surfactant did not have an influence on the % removal of NaCl. The use of surfactant prevented salt powder agglomeration. It formed a thin layer between salt powders. After vulcanization in surfactant-mixed recipe, methanol dissolves the surfactant to allow the continuous space around the rubber particles. Dissolving salts by water can be done more easily as a resulted from the surfactant-inducing space.

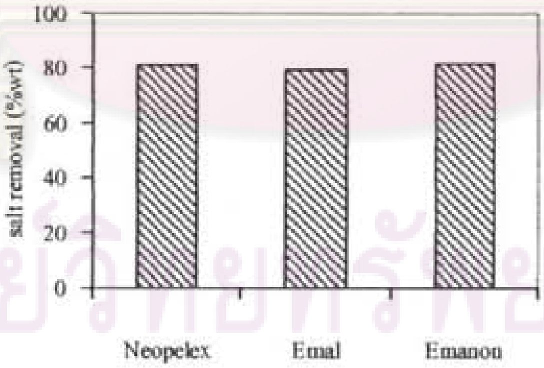


Figure 4.23 Effect of surfactant type combined with NaCl on the salt removal (%wt).

The morphology of sample when using a surfactant combined with sodium salts formulas 7, 8 and 9 was shown in the Figures 4.24-4.25. Figure 4.24 showed

SEM before washing. The anionic surfactant (Neopelex F-50 and Emal 270TH) forms a thin layer interface between NaCl salt powder and the rubber. The micrograph shows salt particles enclosed by the surfactant are characterized of nested small balls. Salt mixed with Emanon is different. Surfactant is fine particles mixed together with the rubber, while some encompassed the sodium chloride particles.

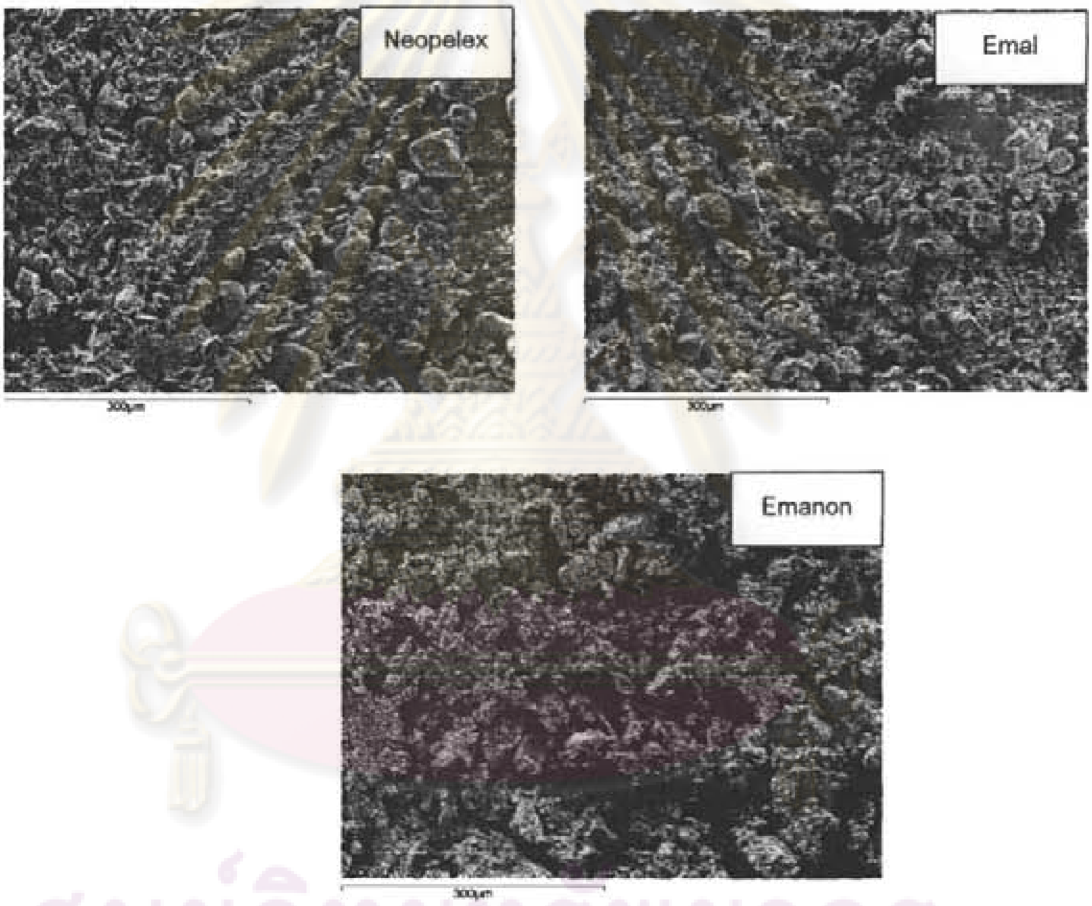


Figure 4.24 SEM micrographs of the fracture of NaCl combined with surfactant types filled NBR cured before salts removal (200x magnification).

It was found that Neopelex F-50 provided thicker sponge cell wall than Emal 270TH. The character of cell wall was affected by the percent volatile matter of surfactant. In the case of Emanon, non-ionic surfactant, cell wall was thicker than the other two surfactants, as Emanon has only 1% volatility, the system viscosity increases. [Figure 4.25] Therefore Emanon cell wall was very strong.

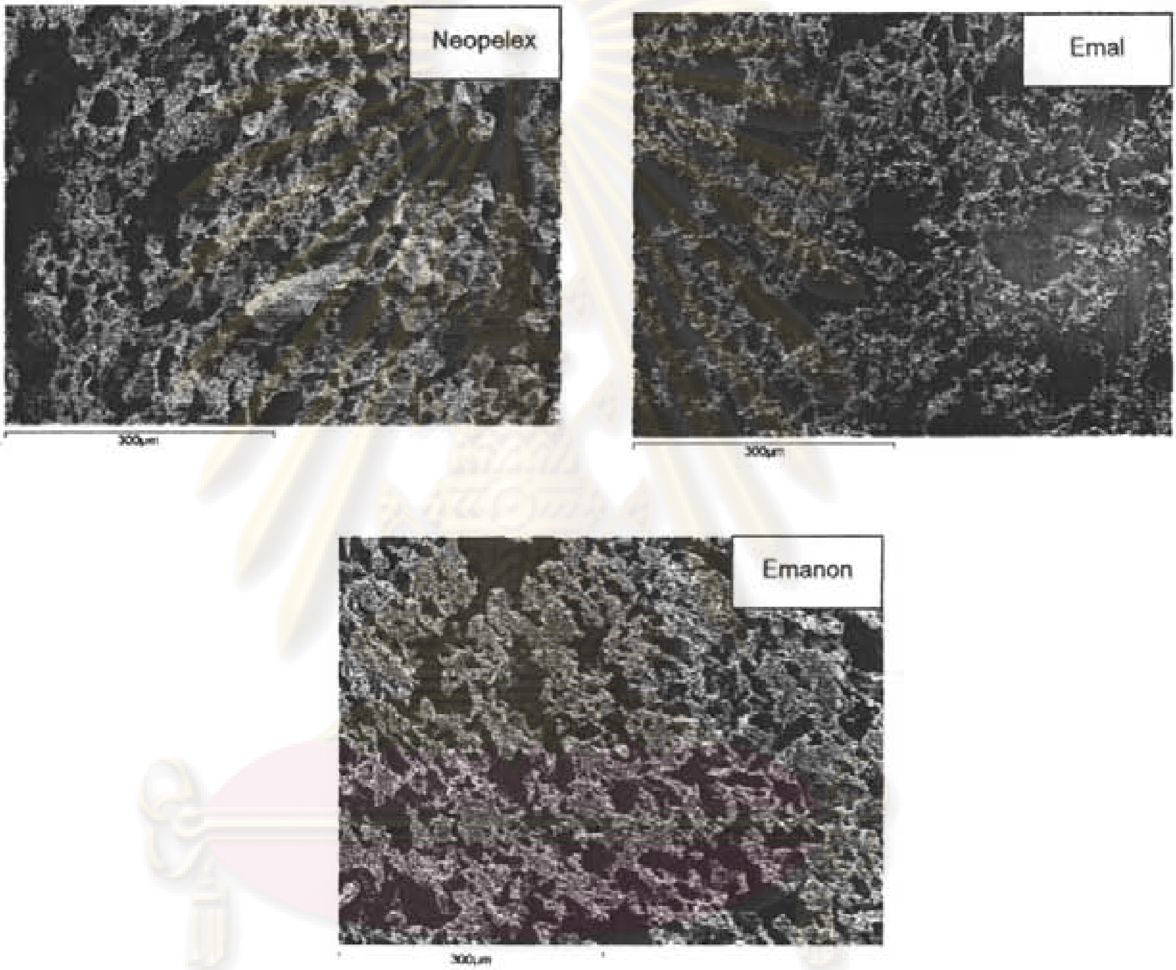
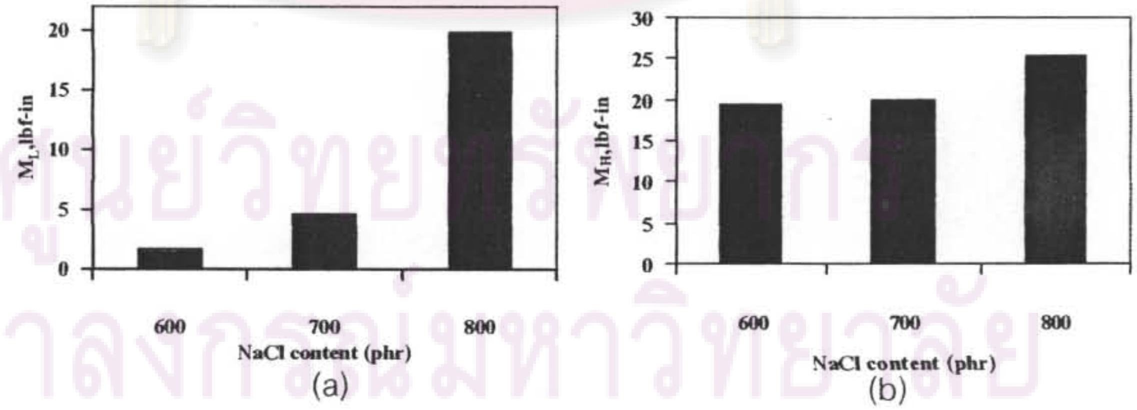


Figure 4.25 SEM micrographs of the fracture of NaCl combined with surfactant types filled NBR cured after salts removal (200x magnification).

4.1.5 Effect of particle size of NaCl mixed surfactant on property of sponge rubber

Formula 10 and 11 are compared to find optimum NaCl content when mixed with Emal. The formula are shown in Table A.3. Emal is used to determine effect of NaCl particle size on removal weight because Emal has minimum torque, M_L about 20 dn.m, the same as pure NaCl compound rubber. Emal mixed NaCl compound rubber can be pressed into the mould perfectly. The less minimum torque, M_L caused compound rubber sticks the mold because higher softy. Scorch time of Emal was between Neopelex and Emanon, and it's cure time value is equaled to Emanon that was 23 min.

Formulas 10 and 11 are compared, effect of particle size of salt-mixed Emal on rubber compound property, as shown in Figure 4.26. In Figure 4.26, when varying NaCl contents, it was found that the minimum and maximum torques of the sample with 800 phr NaCl were the highest. This demonstrates that the higher amount of rigid salt in the system yields more resistance to rheometric torque.



(a) (b)

Figure 4.26 Effect of Emal by variation of sodium content on minimum torque (a) and maximum torque (b).

The effect of salt content in Emal of formula 10 and 11 was study by determine the removal salt ability, as shown in Figure 4.24. When the sodium chloride system was blended with the surfactant: Emal, it also exhibited highest salt removal(%wt). The washing time is decreased from 15 hours to 3 hours when surfactant was mixed with NaCl. The content of salt had no effect on the removal amount as shown in Figure 4.27.

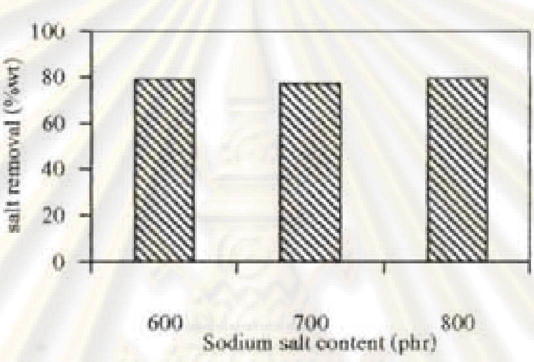


Figure 4.27 Effect of NaCl content combine Emal on salt removal.

The step of salt removal is shown in Figures 4.28-4.30. First, surfactant thin film No.3 was dissolved using the solvent, inducing the continuous space No.4 (see Figure 4.29). Next, water was drained to dissolve salt No.2, inducing the space No.5 in the rubber No.1 (see Figure 4.30).

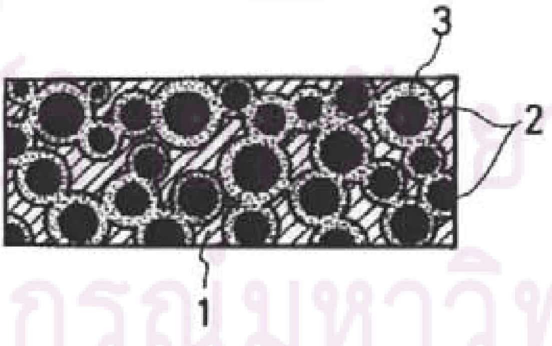


Figure 4.28 The sectional view showing after shaping vulcanization.

rubber constituent 1, the salts powder 2 and a surfactant 3 [10].

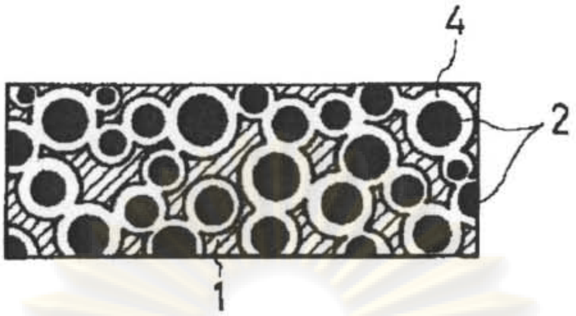


Figure 4.29 The sectional view after removing a surfactant, as it becomes the path 4 of the solvent [10].

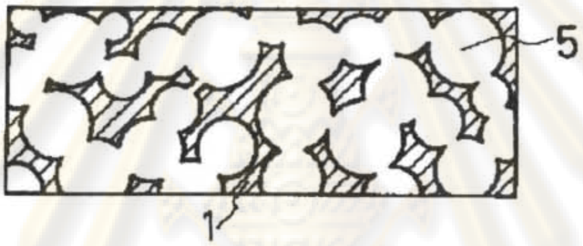


Figure 4.30 The sponge rubber with the open cell 5 is formed [10].

The morphology of compounds filled with different amounts of sodium salts depended on the overlap of holes between salt particles. Noted that the black cavity emerging between the nested salt particles. The solvent reaches the salts powder quite completely when increasing the salt content, since the overlap in the case of 600 phr NaCl was more than those of 700 and 800 phr NaCl. Among of them, NaCl 800 phr provides the thinnest cell with the highest hole connection.[Figure 4.31 and Figure 4.32]

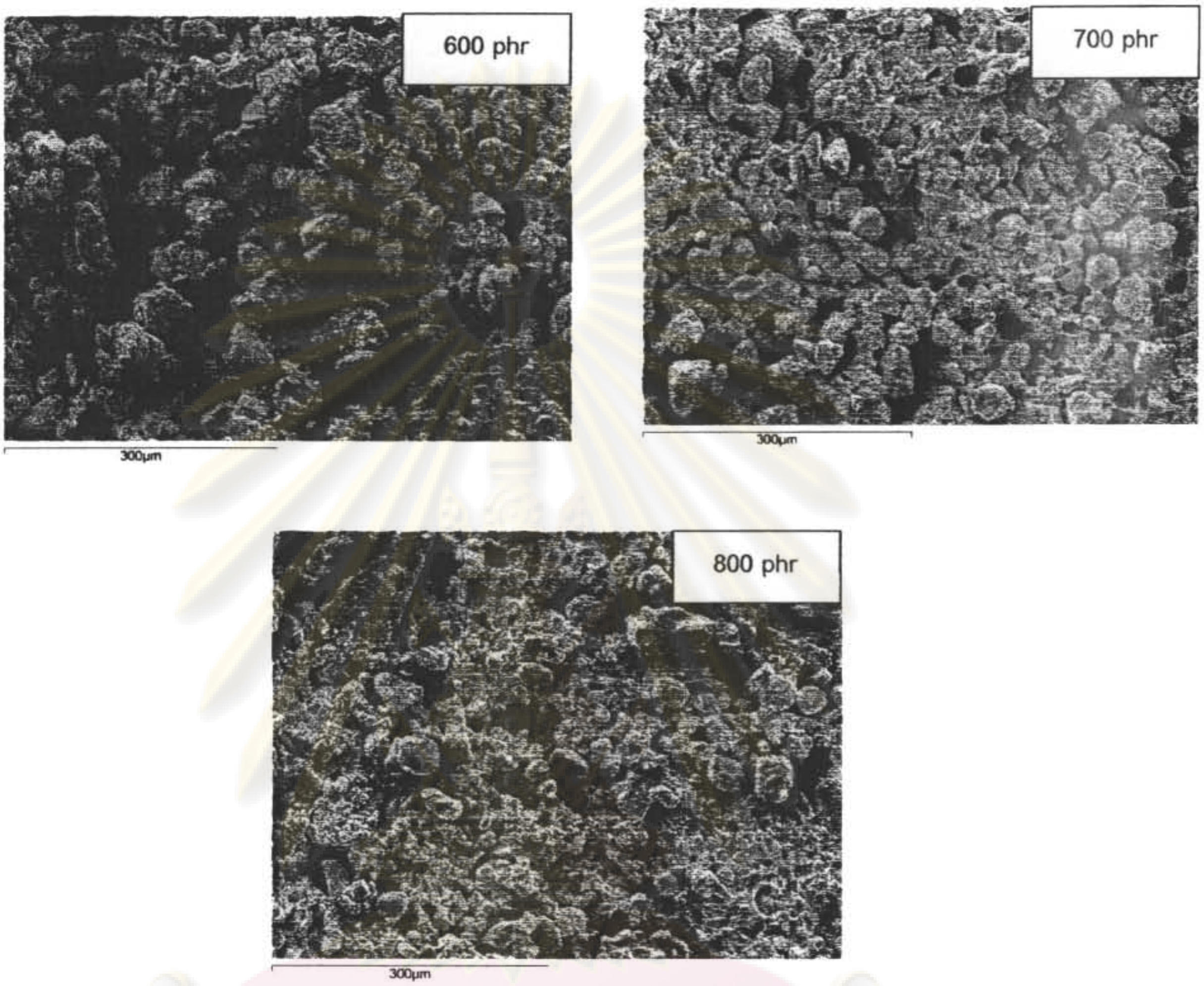


Figure 4.31 SEM micrographs of the fracture of rubber NaCl combined with Emal by various NaCl content (200x magnification).

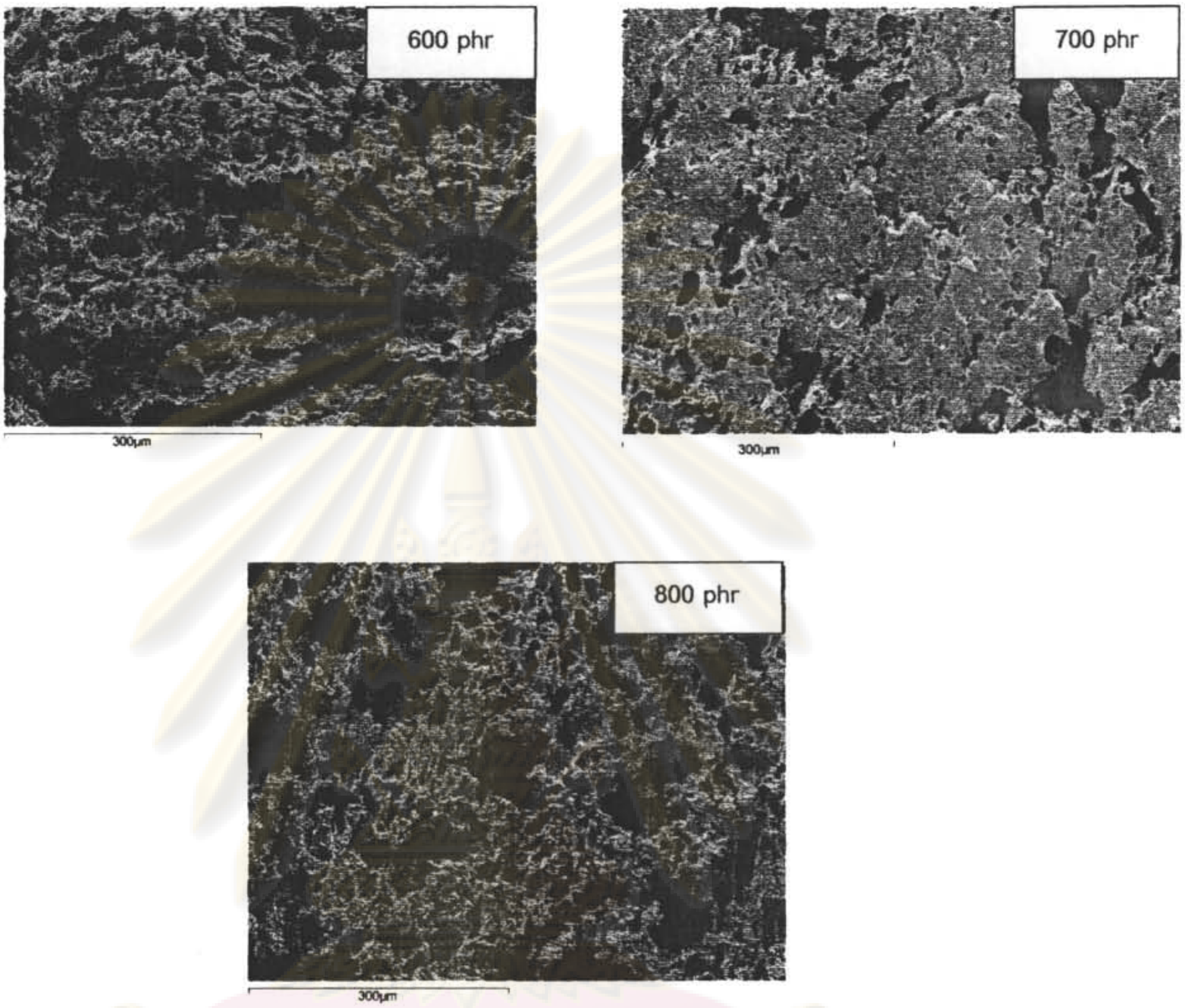


Figure 4.32 SEM micrographs of the fracture at various NaCl content combined with Emal after salts removal (200x magnification).

4.2 Preparation of sponge rubber from $NaNO_3$ and $NaNO_3$-surfactant

From the data of NaCl vulcanizates form open cell in section 4.1, it was found that formulas 2-6 can be used for further improvement by using $NaNO_3$ in place of NaCl, (formulas 1-5 in Table A.4). The effects on sponge rubber were shown in Figure 4.33 Three formula of $NaNO_3$ surfactant (formula 6, 7 and 8) were compounded for the study. The formulas of sponge rubber from $NaNO_3$ were mixed surfactant, as shown in Figure 4.34 $NaNO_3$ was more soluble than NaCl. Then sponge rubbers are checked for printing application.

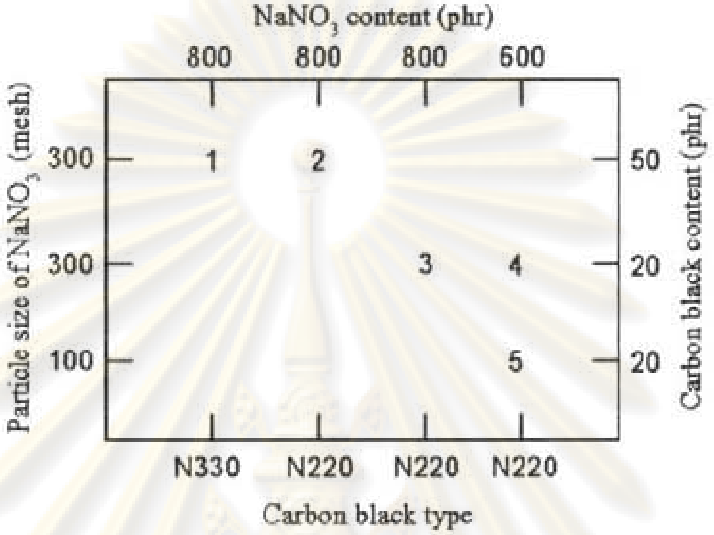


Figure 4.33 Formulation of $NaNO_3$-rubber vulcanizates.

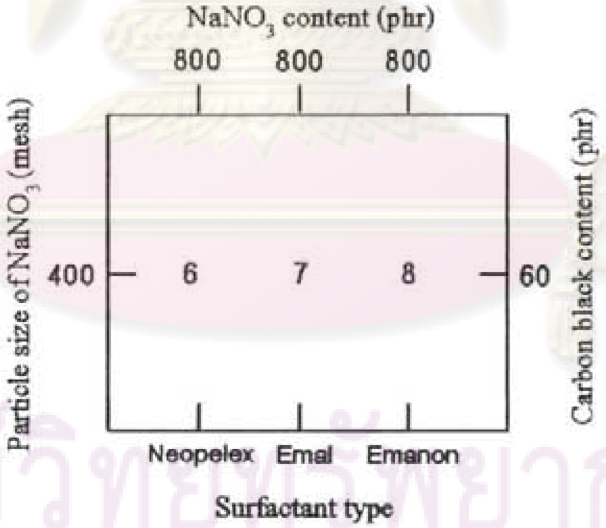


Figure 4.34 Formulation of $NaNO_3$ mixed surfactant in rubber vulcanizates.

4.2.1 Effect of carbon black type on property of sponge rubber

Formula 1 and 2 are compared effect of carbon black type. Carbon black type N-330 and N-220 are used in formula 1 and 2. The sodium salt was washed out from the rubber vulcanizates in the ultrasonic cleaner at 60 °C for 3 and 5 hours for $NaNO_3$ (shorter period of time than that used in the case of NaCl) and then dried at 40 °C in an oven. The effects of carbon black type on the salt removal from rubber are presented in Figure 4.35. The morphology from SEM are presented in Figure 4.36.

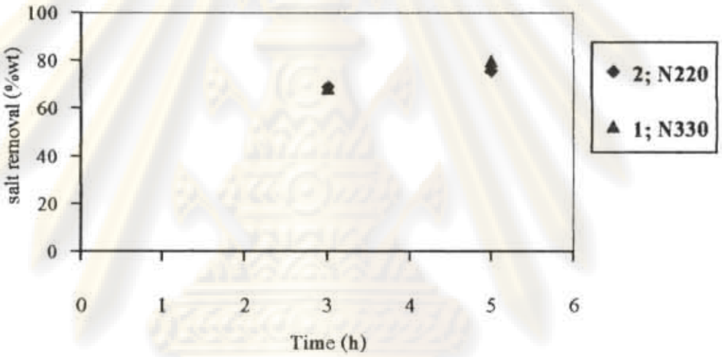


Figure 4.35 Effect of carbon black types on the removal percent weight of $NaNO_3$ from the rubber composite.

From Figure 4.35, the results show that the type of carbon black has no effect on the removal of salts for $NaNO_3$ filled in rubber case. In Figure 4.36, the carbon types have no effect on the appearances of sponge rubbers. $NaNO_3$ can form open cell rubber.

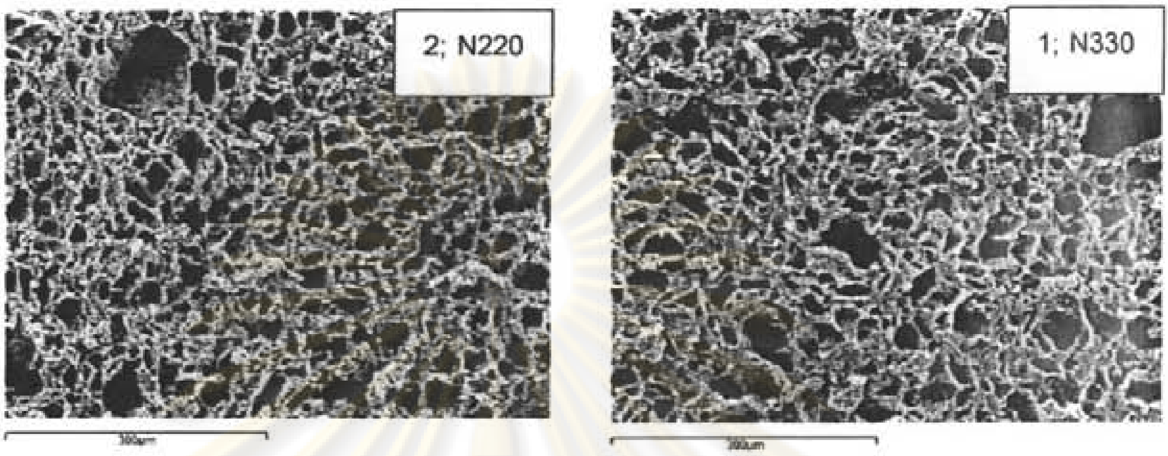


Figure 4.36 SEM micrographs of the fracture of vulcanizates $NaNO_3$ with various carbon black types after removal of salts (200x magnification).

Effects of carbon black type of $NaNO_3$ on the minimum torque, M_L and maximum torque, M_H are shown in Figure 4.37. For the $NaNO_3$ filled compound, the same result is obtained, as shown in Figure 4.7 (NaCl).

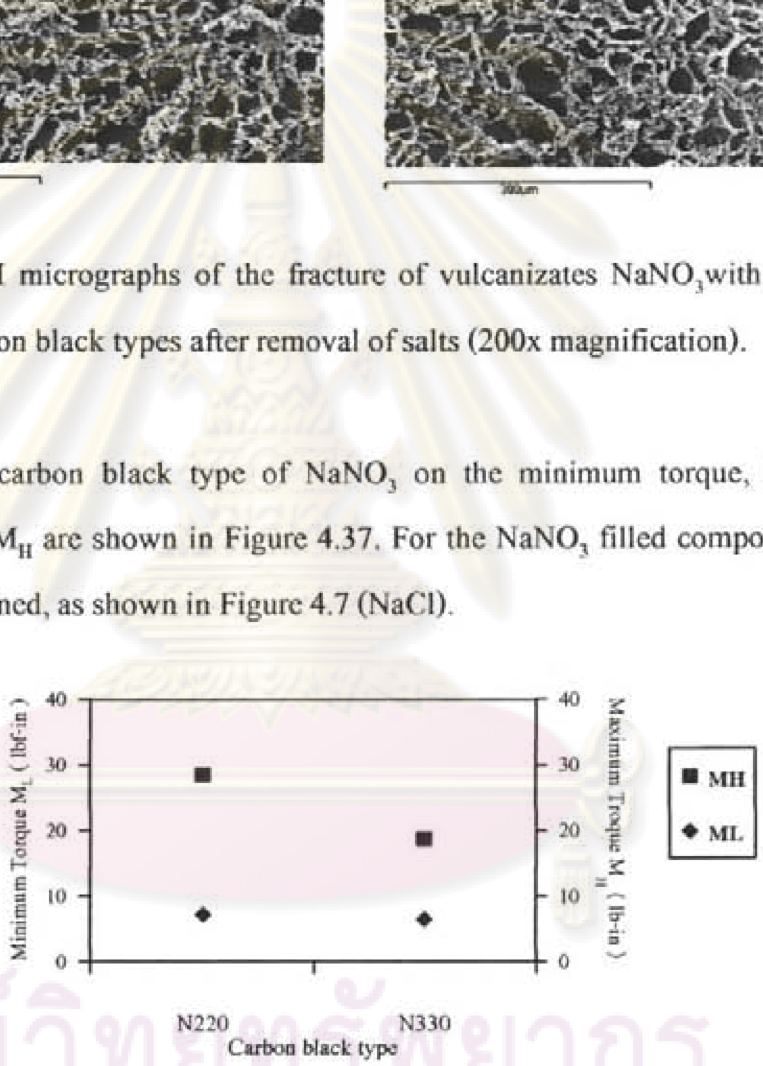


Figure 4.37 Minimum torque, M_L and maximum torque, M_H of $NaNO_3$-rubber compound at different carbon black type.

4.2.2 Effect of carbon black content on property of sponge rubber

Formula 2 and 3 are developed to compare effect of carbon black content. In formula 2, the rubber compound was mixed with 50 phr carbon black. Furthermore, the carbon content will be change to 20 phr carbon black in formula 3. For the effect of carbon black contents, in Figure 4.38, the rubber vulcanizate having 20 phr carbon black gave higher %removal weight than the sample with 50 phr carbon black. In Figure 4.39, the carbon black content have no effect on the appearances of sponge rubbers.

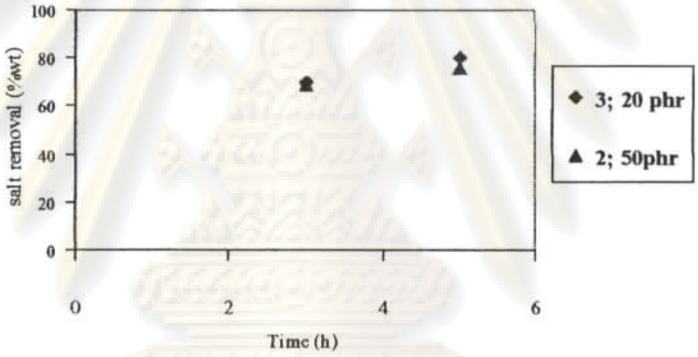


Figure 4.38 Effect of carbon black content on the $NaNO_3$ removal from rubber vulcanizate containing $NaNO_3$ (300 mesh, 800 phr).

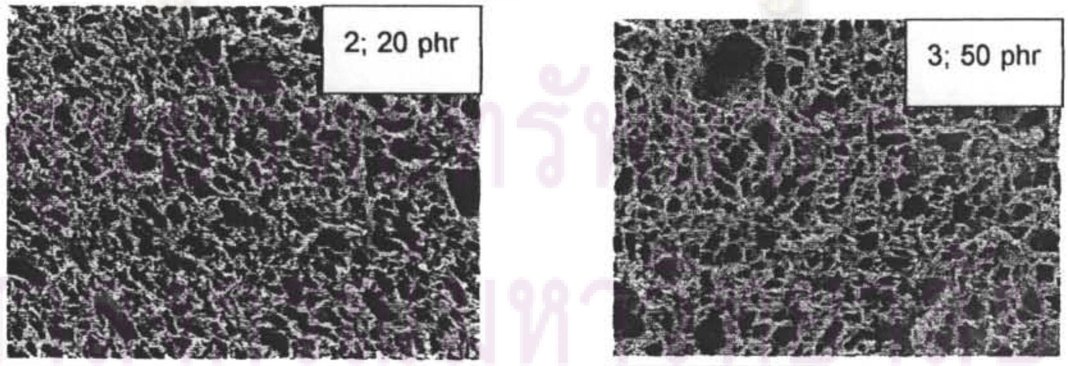


Figure 4.39 SEM micrographs of the fracture of vulcanizates $NaNO_3$with various carbon black contents after removal of salts (200x magnification).

When the N-220 filled blends with various carbon black contents were compared, it was found that the minimum torque, M_L and maximum torque, M_H of rubber with carbon black content of 50 phr was the highest, as shown in Figure 4.40. For the $NaNO_3$ filled compound, the same result is obtained.

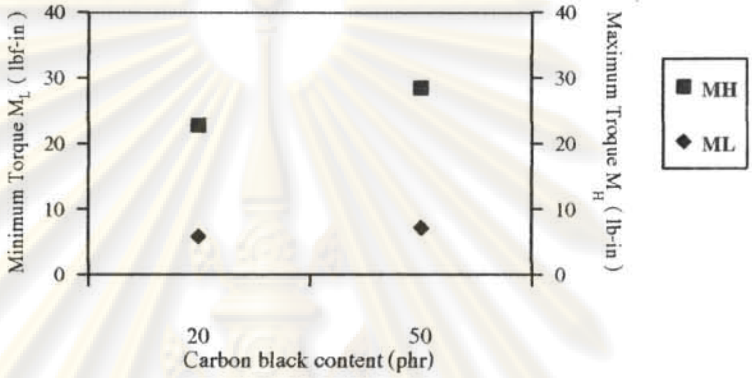


Figure 4.40 Minimum torque, M_L and maximum torque, M_H of $NaNO_3$-rubber compound at different carbon content.

4.2.3 Effect of $NaNO_3$ content on property of sponge rubber

The effect of $NaNO_3$ content was determined by formula 3 and 4. The 800 phr $NaNO_3$ and 600 phr $NaNO_3$ are used. In Figure 4.41, for the effect of amount of sodium salts, it was found that % removal weight of $NaNO_3$ amount of 800 phr was higher than of 600 phr. The increase in size and amount of sodium salts result in more interconnection between the salt particles making sodium salt dissolved more completely.

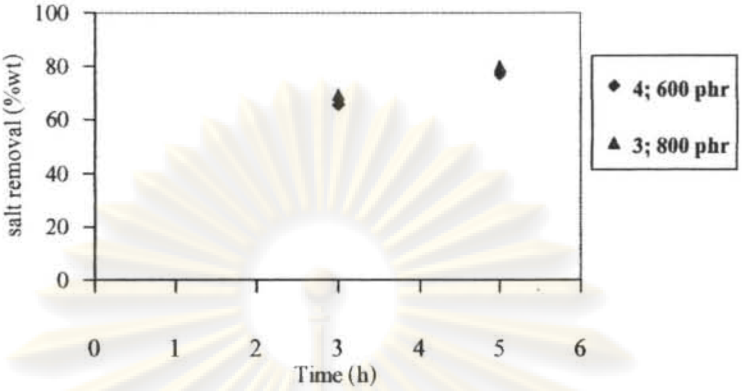


Figure 4.41 Effect of $NaNO_3$ content on removal percent weight of character surface rubber were washed out in the ultrasonic cleaner for 3 h and 5 h and then dried.

The dispersions of sodium nitrate powder and the open pores in the NBR rubber are presented in Figure 4.42. It was found that the open cell content obtained from the sample having 800 phr $NaNO_3$ was more than that of 600 phr. Although the less NaCl content is used at 600 phr but it can form open cell rubber.

In Figure 4.43, for 800 phr content of $NaNO_3$, the minimum torque (M_L) and maximum torque (M_H) was higher than 600 phr because $NaNO_3$ 800 phr gave the highest viscosity.

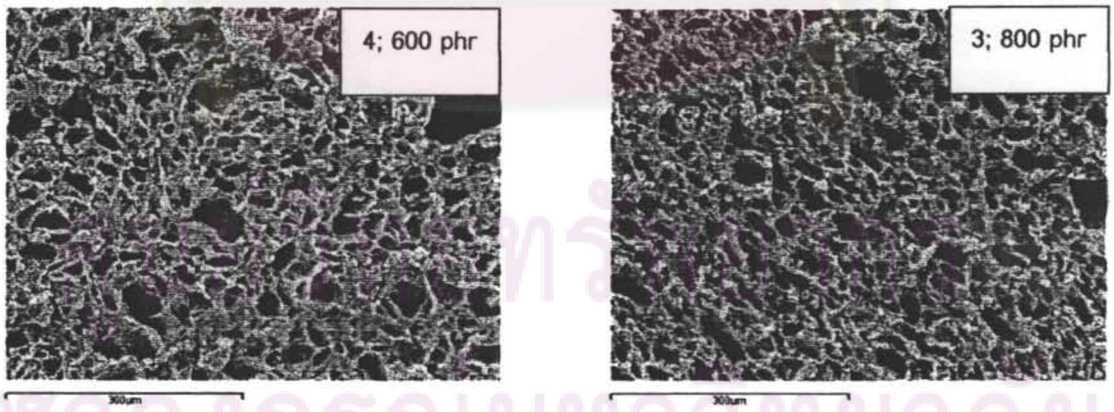


Figure 4.42 SEM micrographs of the fracture of $NaNO_3$ filled NBR vulcanizates containing various contents of salt after removal of salts (200x magnification).

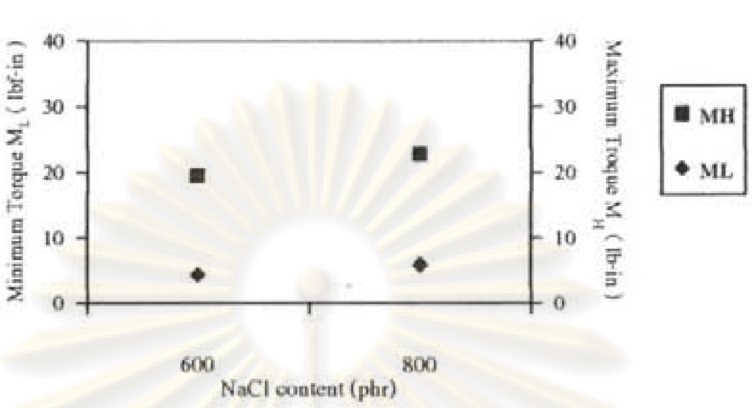


Figure 4.43 Minimum torque, M_L and maximum torque, M_H of $NaNO_3$-rubber compound at different salt content.

In addition, in this work, the scorch time and cure time were measured. The scorch time generally defines as the time for the onset of vulcanization at a particular temperature and thus represents the time available for processing. Cure time is the time required during the vulcanization step for the required amount of crosslinking to occur, yielding the desired level of properties [19].

The scorch times (ts_2) and cure time (tc_{90}) [Figure 4.44] of $NaNO_3$ filled compounds were affected by the content of salts. Among all the tested compositions, the scorch time was the highest for the sample with salt content of 600 phr (fixed at 300 mesh). the same result is obtained, as shown in Figure 4.13 (NaCl).

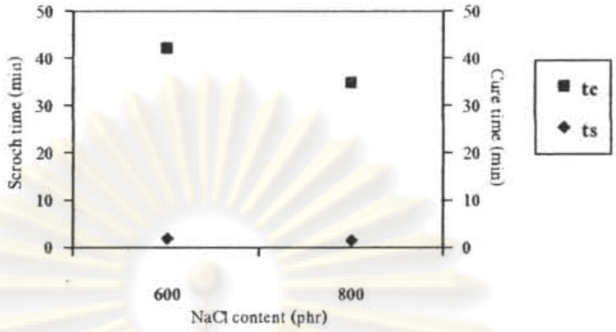


Figure 4.44 Effect of $NaNO_3$ contents on scorch times and cure time of NBR compounds.

4.2.4 Effect of particle size of $NaNO_3$ on property of sponge rubber

Formula 3 and 5 are compared effect of particle size of $NaNO_3$. The 300 mesh $NaNO_3$ and 100 mesh $NaNO_3$ are used. In Figure 4.45, for the effect of particle size of $NaNO_3$, it was found that % removal weight of sodium salt with 100 mesh in size was higher than that with 300 mesh. A similar trend is obtained, as shown in NaCl. Therefore 100 mesh $NaNO_3$ or formula 5 was the most suitable for pre ink stamp product.

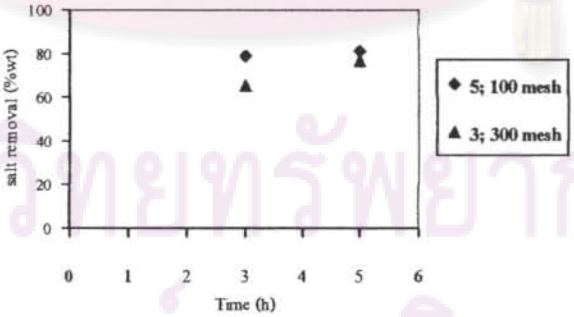


Figure 4.45 Effect of $NaNO_3$ particle sizes on the salt removal of $NaNO_3$ from the character surface rubber that was washed in the ultrasonic cleaner.

The dispersions of sodium nitrate powder and the open pores in the NBR rubber are presented in Figure 4.46. It was found that the open cell formed by the 100 mesh $NaNO_3$ was bigger than that formed by 300 mesh salt. For the $NaNO_3$ filled compound, a similar trend is obtained, as shown in the sponge rubber from NaCl.

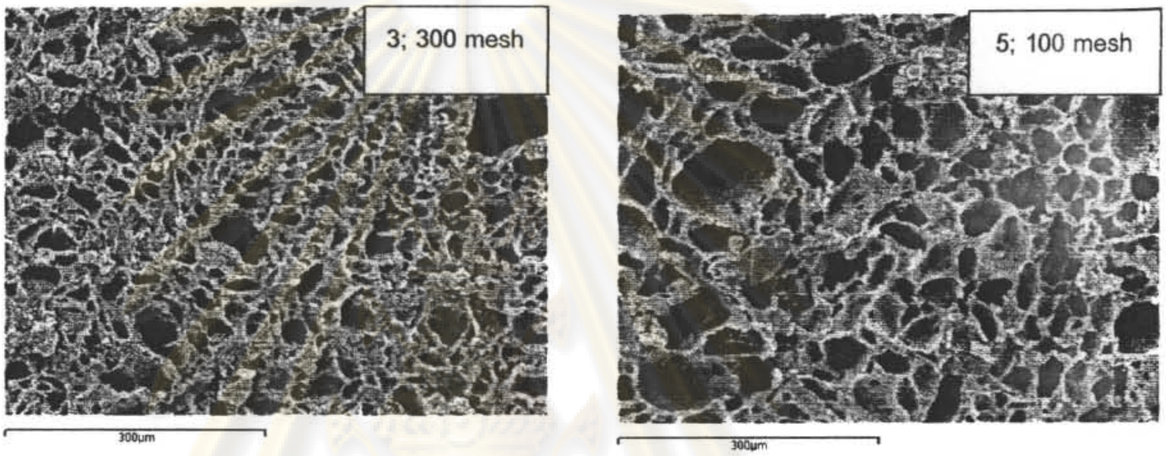


Figure 4.46 SEM micrographs of the fracture of $NaNO_3$ filled NBR vulcanizates containing salts at various with particle sizes after removal of salts (200x magnification).

From the morphology of rubber samples after salt removal in Figure 4.47 (a) and (b) viewed by SEM at x500 magnification, the sample of $NaNO_3$ 100 mesh can form open cell size approximate 50-100 micrometer while in the sample with 300 mesh $NaNO_3$ pores having diameter of 5-50 micrometer were observed. The small pores size had effected on adsorption oil ink, so it's got a less amount of oil ink and increase inking time.

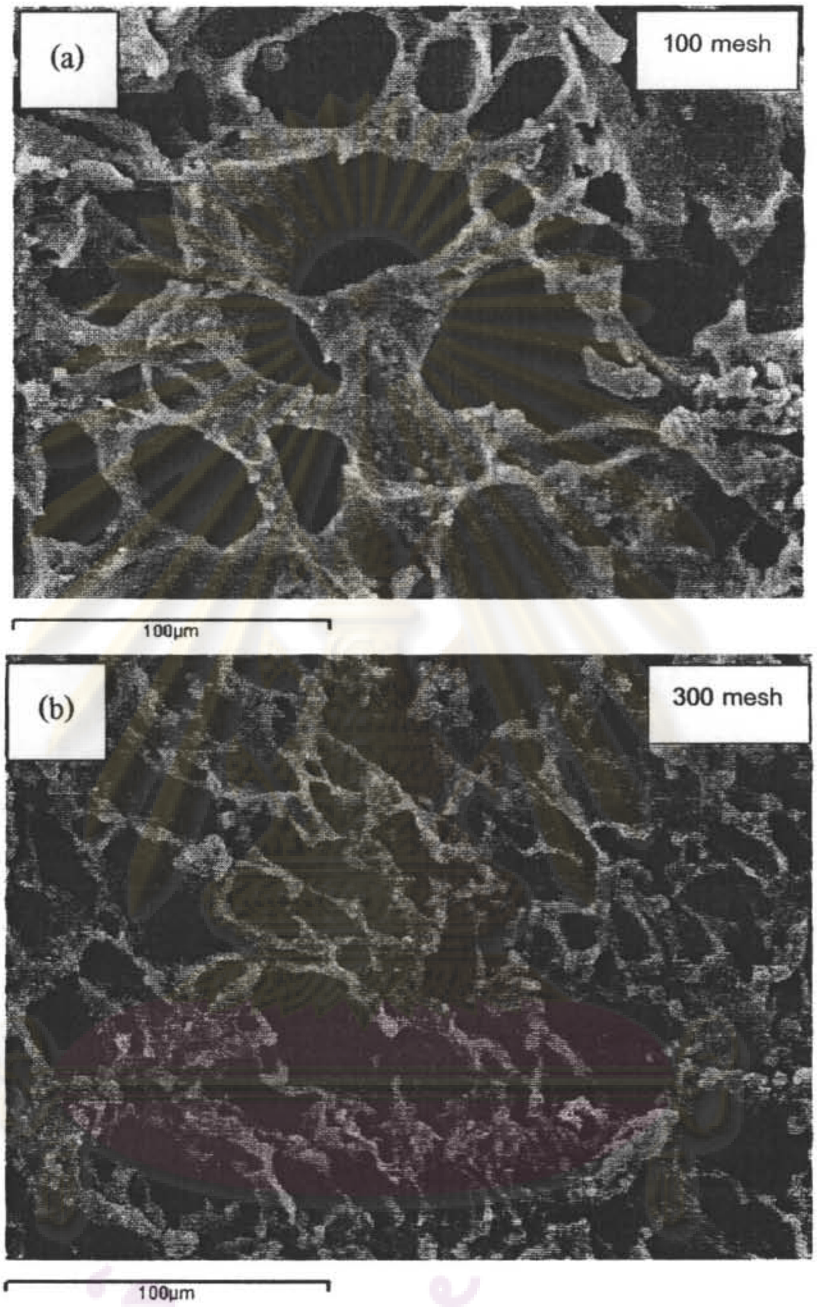


Figure 4.47 SEM micrographs of the fracture of sponge NBR rubber formed by $NaNO_3$:(a) 100 mesh, (b) 300 mesh (500x magnification).

The minimum torque (M_L) and maximum torque (M_H) of $NaNO_3$ filled rubber at 100 mesh (0.144 mm) of salts was the highest, as shown in Figure 4.48.

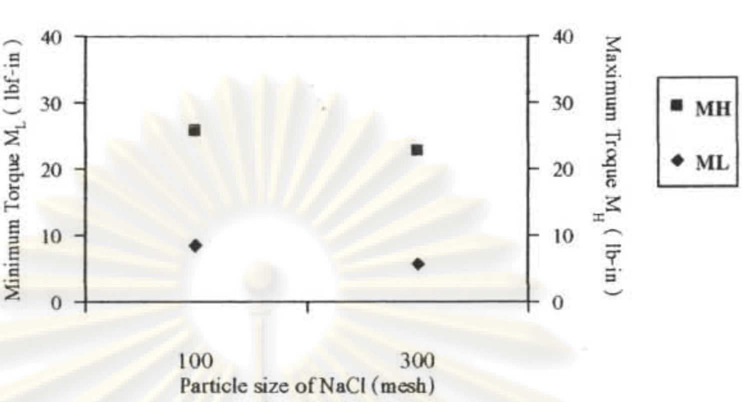


Figure 4.48 Minimum torque, M_L and maximum torque, M_H of $NaNO_3$-rubber compound at different salt particle size.

The scorch times (ts_2) and cure time (tc_{90}) [Figure 4.49] of $NaNO_3$ filled compounds were affected by the particle size. Among all the tested compositions, the scorch time was the highest for the sample with particle size of 100 mesh (fixed at 800 phr). It can be explained that the higher surface area of salts and salts content make the system more viscous, therefore scorch time and cure time were shorten. The test result for such respective formula 5 has shown the scorch time value at 3 minutes, the compound rubber has enough time to flow into the mold before the rubber is hardened.

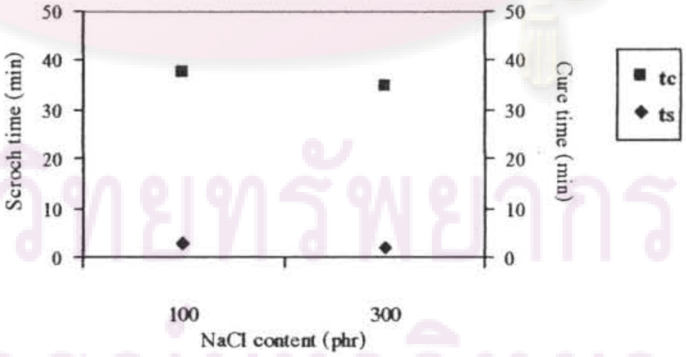


Figure 4.49 Effect of $NaNO_3$ particle size on cure times of NBR compounds.

4.2.5 Sponge rubber from $NaNO_3$-surfactant

For $NaNO_3$ mixed three surfactants, it was found that Emanon-$NaNO_3$; formula 8 can compound and compressed character molding only formula. Because other surfactants have high %volatile, the compound rubber was sticky of mold surface. For Emanon-$NaNO_3$ (formula 8) rubber provided salt removal about 80% weight which was similar to Emanon-NaCl rubber, can see Appendix B. In Figure 4.50 SEM micrograph, it was found that the pore size of $NaNO_3$ was larger. This might effect to the imprint quality.

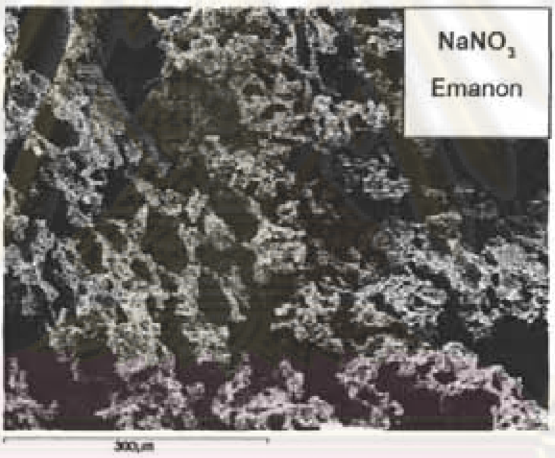


Figure 4.50 SEM micrographs of the fracture of $NaNO_3$ combined with Emanon after salts removal (200x magnification).

In Figure 4.51 the cure time (tc_{90}) of $NaNO_3$-Emanon was the highest because $NaNO_3$ can adsorb humid in air when combined with surfactant, Emanon. Therefore formula 8 of $NaNO_3$ mixed surfactant not suitable for industrial production.

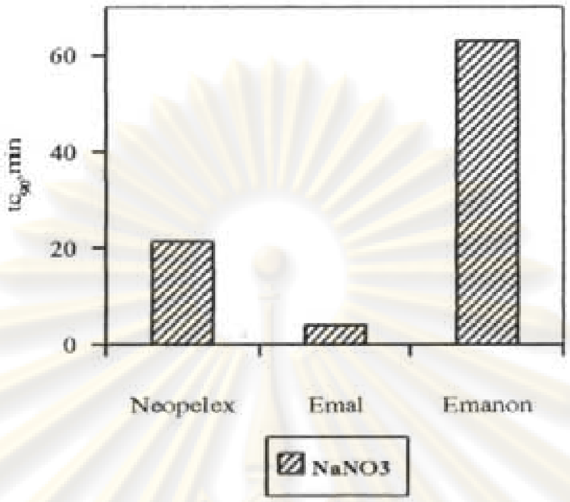


Figure 4.51 Effect of surfactant types on cure time of $NaNO_3$-surfactant.

4.3 Physical properties: Hardness test (ASTM D2240)

Hardness is typically measured as resistance to surface indentation under specific condition, so the force is supplied as a point of compression rather than an area of tension. The hardness value was demonstrated particularly only sponge rubber, which were $NaNO_3$ forming porous structure, NaCl mixed with surfactant and $NaNO_3$ mixed with surfactant.

Hardness value of the sponge rubber from $NaNO_3$

Formula 1 and 2 are compared effect of carbon black type. Carbon black type N-330 and N-220 are used in formula 1 and 2. The effect of carbon black types on the $NaNO_3$ rubber was investigated. It was found that the hardness of compound filled with carbon black type N-220 was higher than that with carbon black N-330 because of the higher surface area (small particle size of N-220), see Figure 4.52.

Formula 2 and 3 are compared effect of carbon black content. The 50 phr carbon black and 20 phr carbon black are used in formula 2 and 3. The spring hardness of sample with 50 phr was higher than that with 20 phr. This might be due to the effect of carbon black content and type.

Formula 3 and 4 are compared effect of $NaNO_3$ content. The 800 phr $NaNO_3$ and 600 phr $NaNO_3$ are used in formula 3 and 4. It found that the sponge rubber formed lower amount of $NaNO_3$ 600 phr gave higher spring hardness than 800 phr. At 600 phr $NaNO_3$ was form open cell lesser than 800 phr $NaNO_3$. The sponge rubbers have more softies, hardness value was less.

Formula 3 and 5 are compared effect of particle size of $NaNO_3$. The 300 mesh $NaNO_3$ and 100 mesh $NaNO_3$ are used in formula 3 and 5. For the sodium nitrate, it was found that the hardness of 300 mesh sample was higher than that of 100 mesh.

Hardness of formula 4 and 2 are not suitable for pre-ink stamp, because of less adsorb of oil ink. Formula 5, is good for pre ink stamp, as it has open cell interconnection and numerous pores.

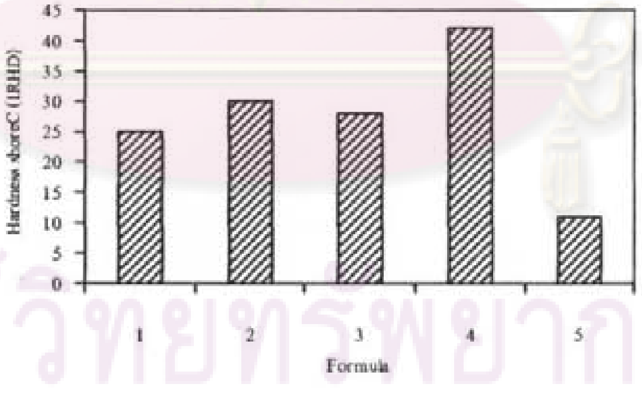


Figure 4.52 Relationship between improvement formulation filled with $NaNO_3$ form sponge rubber with hardness.

Hardness value of sponge rubber from NaCl-mixed surfactant

Formula 7 (Neopelex), 8 (Emal) and 9 (Emanon) shown in Table A.3 were compared effect of surfactant type on hardness of sponge rubber. Figure 4.53 shows the hardness of compound filled with different types of surfactant. It can be seen that the hardness value of the sponge rubber which filled with nonionic surfactant (Emanon 3299R) was lowest. This demonstrates that the surfactant can help the dissolution removal of the powder salt. The sponge rubber softens due to numerous open cells.

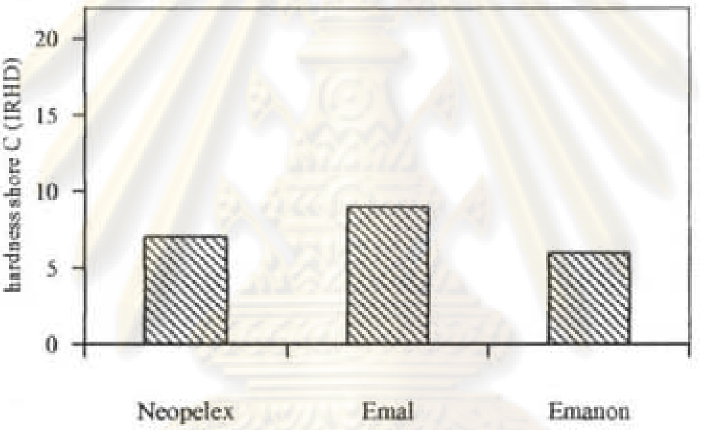


Figure 4.53 Effect of surfactant types on the hardness of smooth surface after NaCl leaching for 3 h.

From these observations, it is clear that in solution, non-ionic surfactant is more surface-active than anionic types, as non-ionic surfactant produce lower surface tensions than anionic surfactants at equivalent concentrations [20]. Also, at comparable hydrophobic chain sizes, non-ionic surfactant form micelles more readily; this is probably because of without an ionic charge there is no barrier to aggregation. One of the advantages of using non-ionic surfactants is that the critical micelle concentration is very low, in the order of 0.05-0.5 g/l in comparison with anionic ones with a critical micelle concentration of 0.5-3 g/l. A surfactant with a low critical micelle concentration gives rise to a washing solution of effective cleaning power at low concentrations [20].

Formula 8 (800 phr), 10 (700 phr) and 11 (600 phr) are shown in Table A.3. The effect of NaCl content are compared when mixed Emal 120 phr on hardness.

In Figure 4.54, the hardness of smooth surface at 600 and 800 phr were not different. Thus, the effect of the salt partial content for 600 and 800 phr could be neglected when surfactant was added into the rubber compound.

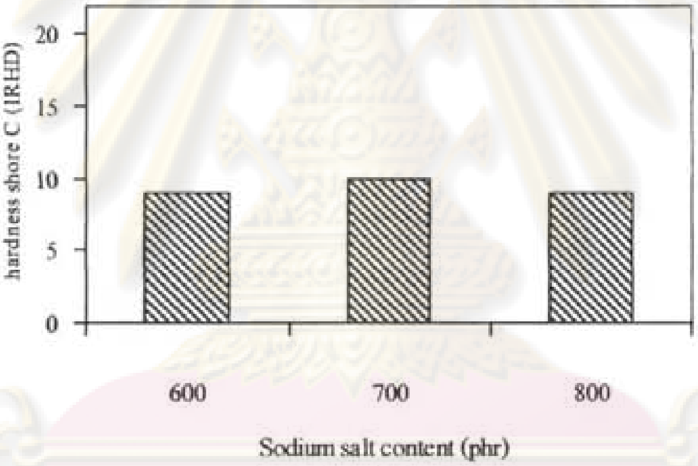


Figure 4.54 Effect of NaCl content on the hardness of Emal-rubber that was washed out for 3 h in the ultrasonic cleaner.

When compare the type of salt at the same surfactant, Emanon, and similar removal time (3 hr), it was found that the hardness of the sponge $NaNO_3$ rubber was lower than 1 IRHD. This was not significantly different from NaCl rubber, as shown in Table B.1.

In present study, hardness value of the opened-cell sponge rubber is within arange 5-25. NaCl mixed with surfactant showed hardness value of 5-10. Emanon is regarded optimal formula (formula 9 in Table A.3). $NaNO_3$ forming porous structure provides the hardness value of 11-25. $NaNO_3$-100 formula 5 in Table A.4 is optimal formula.

4.4 Adsorption of oil ink

Adsorption of ink of the sponge rubber material was checked. [Figures 4.55-4.61]. The viscosity of oil ink was 15-30 centipoises (25 °C). In this study, the oil ink absorption was tested by using two methods, absorption oil ink weight and absorption oil ink time.

4.4.1 Absorption weight of sponge rubber from $NaNO_3$ and NaCl-surfactant

$NaNO_3$- sponge rubber

Absorption oil ink weight, the permeated ink weight was determined. The ink was filled into the sponge rubber, ink filling rate was 1 drop/min and the filling time was one hour. The result has suggested that if ink weight is higher, it represents higher absorption, which is benefit for reducing the absorption stage in the production process.

Formula 1 and 2 are compared to present effect of carbon black type, formula 1 added carbon black type N-330 while formula 2 was added N-220. $NaNO_3$ could offer the open cell sponge rubber without surfactant. The effect of type and quality of carbon black, and type and amount of salt, were shown in Figure 4.55. Absorption weight of oil ink weight of N-330 carbon black was higher than N-220 carbon black.

Formula 2 and 3 are compared effect of carbon black content. The 50 phr carbon black and 20 phr carbon black are used in formula 2 and 3. If carbon content was reduced, the absorption amount was increased. Furthermore, amount of oil ink was very low when the sponge rubber was produced by 50 phr carbon black.

Formula 3 and 4 are compared effect of $NaNO_3$ content. The 800 phr $NaNO_3$ and 600 phr $NaNO_3$ are used in formula 3 and 4. Figure 4.56 presented the effect of salt contents on porosity in sponge rubber. It was shown that ink was not adsorbed into sponge rubber of 600 phr salt since the porosity or hold connection in rubber was not high enough.

Formula 3 and 5 are compared effect of particle size of $NaNO_3$. The 300 mesh $NaNO_3$ and 100 mesh $NaNO_3$ are used in formula 3 and 5. Larger salt particle sizes provide higher absorption amount.

Even without filling the surfactant, using only $NaNO_3$ to form the porosity, salt can be removed from rubber effectively, but the ink adsorption rate of sponge is so slow, about 0.47-1.34 g/hr, as shown in Figure 4.56. The optimum sponge rubber formulas on absorption ink are formula 1, 3 and 5. Formula 5 can absorb the most weight of ink of time spent within 1 h.

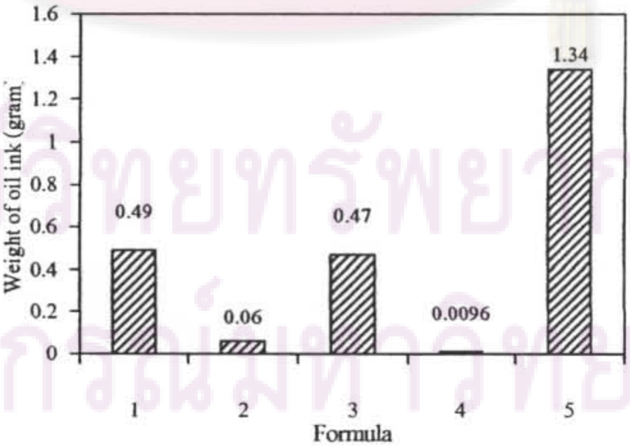


Figure 4.55 Relationship between improvement formulas of sponge rubber from $NaNO_3$ with weight of oil ink.

NaCl- surfactant sponge rubber

Formula 7 (Neopelex), 8 (Emal) and 9 (Emanon) shown in Table A.4 were compared effect of surfactant types on absorption oil ink weight of sponge rubber. Among the various surfactant types which used to help washing out sodium chloride salt from the rubber, the weight of oil ink was the highest for Neopelex blend and lowest for the Emal blend [Figure 4.56].

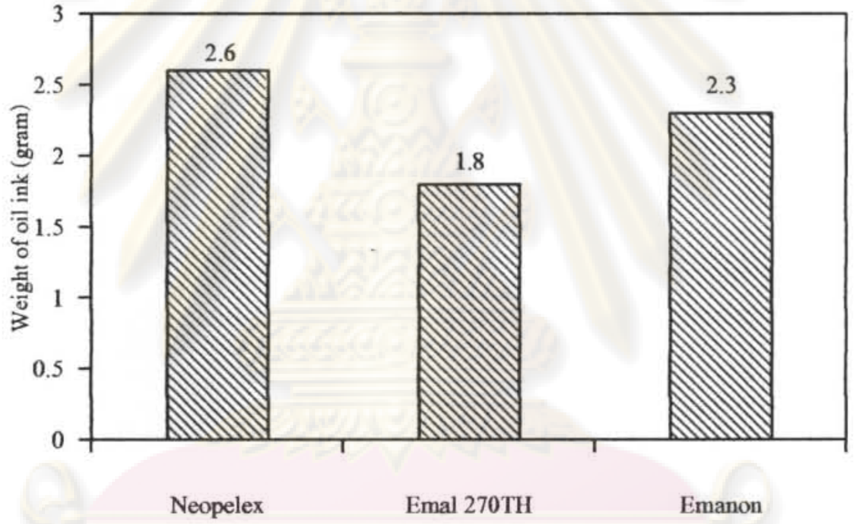


Figure 4.56 Weight of oil ink after inking on sponge rubber for 1 h, effect of surfactant type combined with NaCl.

For blending surfactant with sodium chloride, it was found that the Emanon gave the best compound rubber. Emanon contains 1% volatile matter (water) which less than other surfactants. Thus, it is suitable for the mixing process. Furthermore, the cured product was still a solid state enough to press character surface in the vulcanization process. In case that the cure product too soft, it difficult was to press unvulcanizates rubber formed character surface in the mold. The rate of ink adsorption was 2.3 g/hr.

Formula 8 (800 phr), 10 (700 phr) and 11 (600 phr) shown in Table A.4 were compared effect of NaCl content mixed with Emal 120 phr on absorption oil ink weight of sponge rubber. In Figure 4.57, the highest absorption velocity was provided by 800 phr. sodium, 2.2 g/hr. This might be the effect of porosity of sponge rubber which depended on the salt content in rubber compound. The optimum formula for sponge rubber to form NaCl-surfactant was formula 9. The optimum salt content was 800 phr.

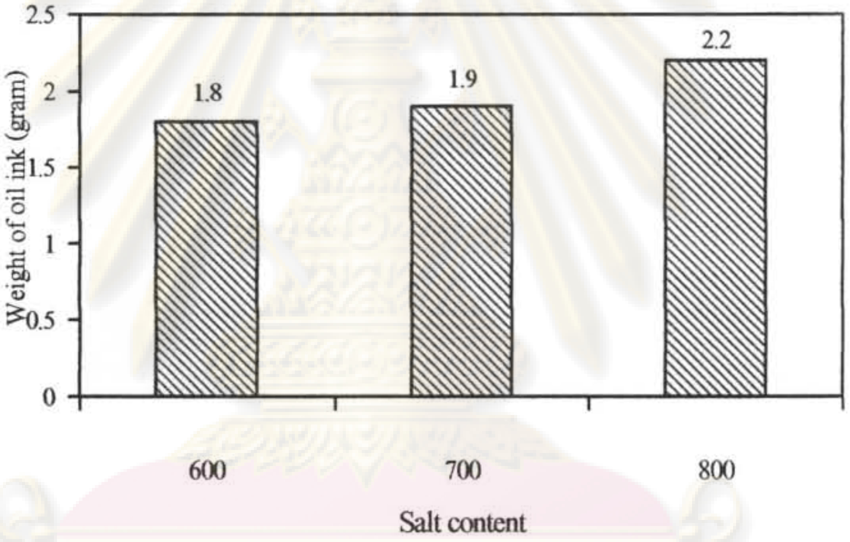


Figure 4.57 Weight of oil ink after inking on sponge rubber for 1 h, effect of NaCl content in Emal surfactant.

4.4.2 Absorption time of sponge rubber from $NaNO_3$ and NaCl-surfactant

$NaNO_3$- sponge rubber

Absorption oil ink time was the first time of inking. Production is required short time of adsorption of ink. The investigation of ink absorption time was shown in

Figure 4.58 and Figures 4.60-4.61. Five difference formulas were set to produce sponge rubber $NaNO_3$ without surfactant. It was found that the accepted absorption rate of sponge rubber was achieved from only three formulas. The unaccepted absorption rate was 0.0593 and 0.0096 g/hr. Sponge rubber with high capacity of ink absorption at slightest filling time is a high quality sponge rubber.

Rate of absorbed ink weight per hour for sponge rubber from $NaNO_3$ is 0-1.3 g/hr; (Formula 2 and 4 as shown in Table A.4, ink weight absorption was fails due to too high viscous ink), and sponge rubber applying surfactant mixed with NaCl will yield ink weight absorption range at around 1.8-2.6 g/hr.

Formula 3 and 5 are compared to find effect of particle size of $NaNO_3$. The 300 mesh $NaNO_3$ and 100 mesh $NaNO_3$ are used. The higher partial size resulted in lower absorption time since the larger connection holds size, shown in Figure 4.58. The total absorption time was 72 min. In formula 1, the ink absorption time of $NaNO_3$ sponge rubber was 95 min. This was not benefit for actual production.

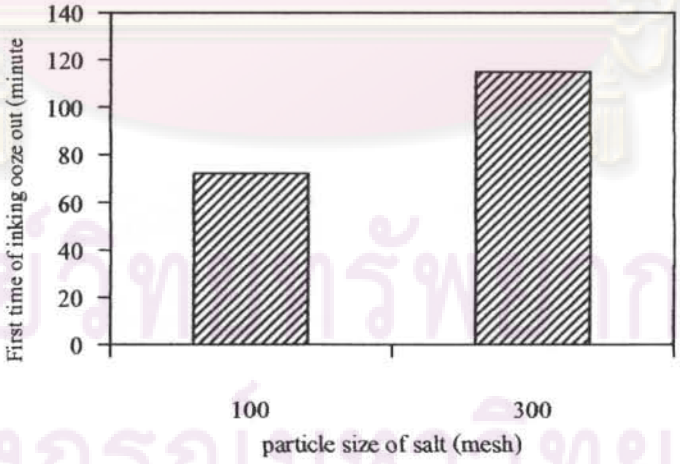


Figure 4.58 Effect of $NaNO_3$ particle size on the first time were detected, when ink ooze out on paper.

Inking for $NaNO_3$ system required long time because there are less interconnection between their open cells. If these cells have a lot of interconnect, the sponge was high ink absorption characteristics. Rubber generated by $NaNO_3$ producing the porosity takes longer filling time. In pre ink application process, we have to wait until the former ink was adsorbed completely before usage. The interconnection of cell is shown in the Figure 4.59.

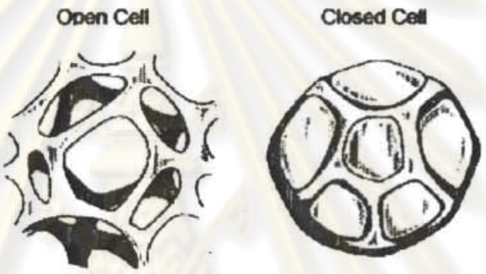


Figure 4.59 Distinctness of closed cell and open cell were the open cell has interconnection cells. The closed cells, which do not collapse, losing air as in open cell sponge [21].

NaCl- surfactant sponge rubber

Formula 7 (Neopelex), 8 (Emal) and 9 (Emanon) shown in Table A.3 were compared surfactant type on absorption oil ink time spent of sponge rubber. The rubber compound with Emanon shows the fastest rate of inking ooze out. This is due to the fact that the Emanon is a nonionic surfactant, as shown in Figure 4.60. Neopelex use the first time of inking the highest at 36 min is not recommended to be comercial. Emanon gave good productivity. Longer time ink filling process results in higher production cost.

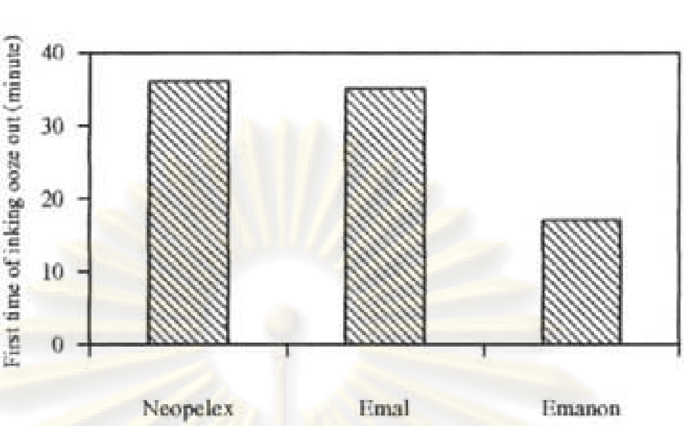


Figure 4.60 Effect of surfactant type on the first time were detected, when ink ooze out on paper.

Formula 8 (800 phr), 10 (700 phr) and 11 (600 phr) shown in Table A.4 were compared effect of NaCl content mixed with Emal 120 phr on absorption oil ink time spent of sponge rubber. The 800 phr salt content offered the highest absorption time. Thus, absorption time was depended on salt content in the rubber, as shown Figure 4.61.

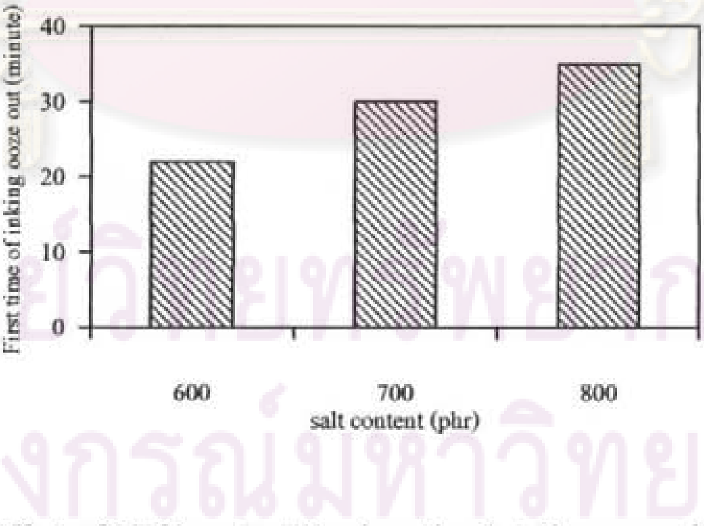


Figure 4.61 Effect of NaCl content-Emal on the first time were detected, when ink ooze out on paper.

At the same surfactant, Emanon, the absorption time of two type of salt, NaCl and $NaNO_3$, was compare together. It was found that the lower absorption time NaCl is 17 min and 20 min for $NaNO_3$. Upon test results, found that $NaNO_3$ filled in rubber formula 5 (Table A.4) represents the optimal ink absorption using single $NaNO_3$ solely, while NaCl-mixed surfactant for sponge rubber is Emanon, formula 9 in Table A.3.

4.5 Impression test

Sharpness and clear impression are important in this study. The impression test indicated the quality of imprint when it was used continuously. Comparison the number of imprints were possible and checked durability of wear and tear, sharpness of contours.

Impression test is employed to test the capacity of sponge rubber in respect of the optimal pre ink. The results displayed high resolution and high capacity in transferring the printing ink continuously, and able to identify the characteristics of the pressed alphabet rubber effectively.

$NaNO_3$-sponge rubber

Figure 4.62 shows the best quality of imprints, effect of particle size of $NaNO_3$ filled in the compound rubber. For $NaNO_3$, at particle size 100 mesh formula 5 gave the best quality of imprints. But when compared the time of inking, NaCl-Emanon; formula 9 oozed faster than $NaNO_3$-100 mesh; formula 5.

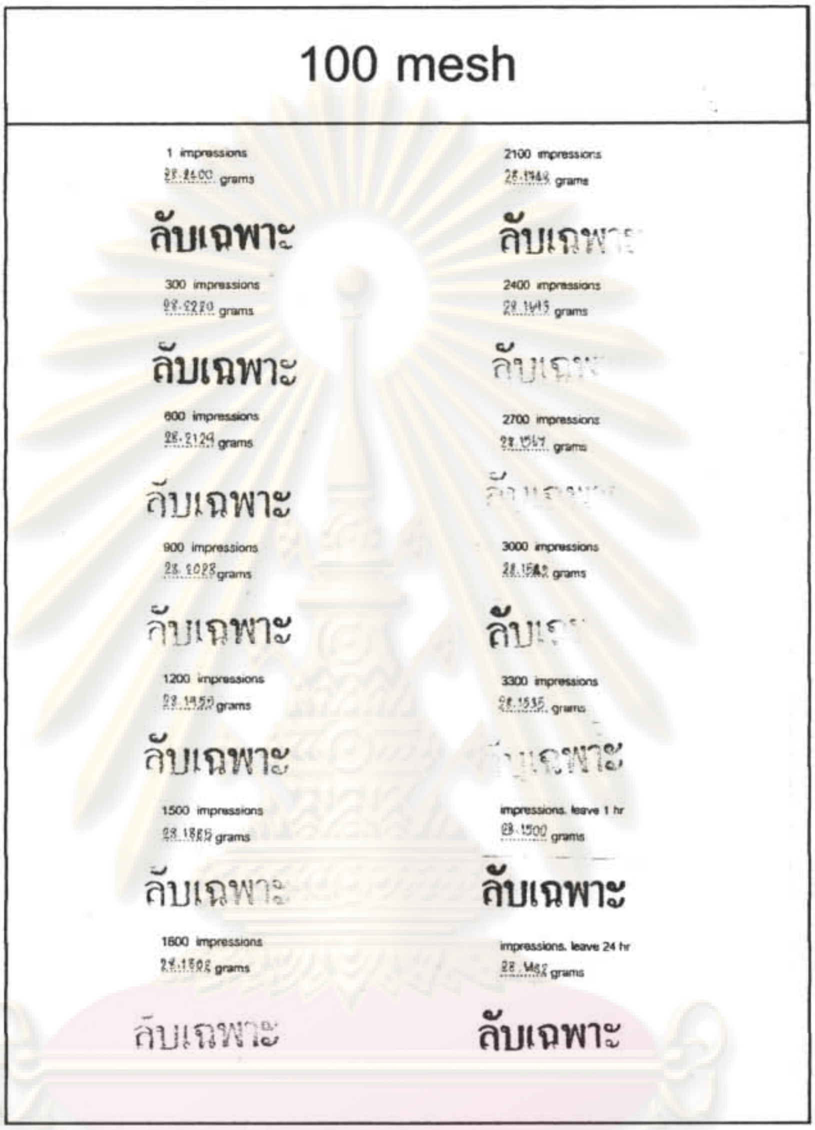


Figure 4.62 Quality of imprints and number of imprints of $NaNO_3$ particle size 100 mesh, formula 5.

NaCl-surfactant sponge rubber

Figure 4.63 shows quality of imprints, effect of surfactant type filled in the NaCl compound rubber compared with Xstamper® in Figure 4.64.

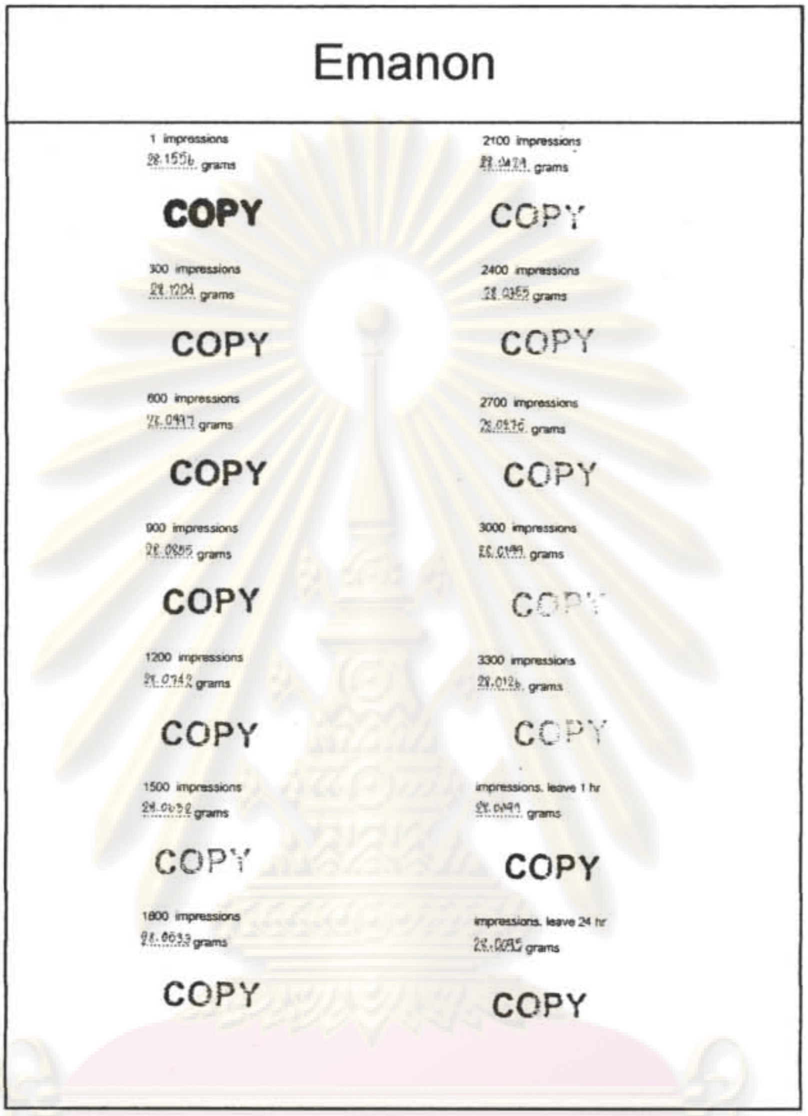


Figure 4.63 Quality of imprints and number of imprints of sodium chloride mixed Emanon; formula 9.

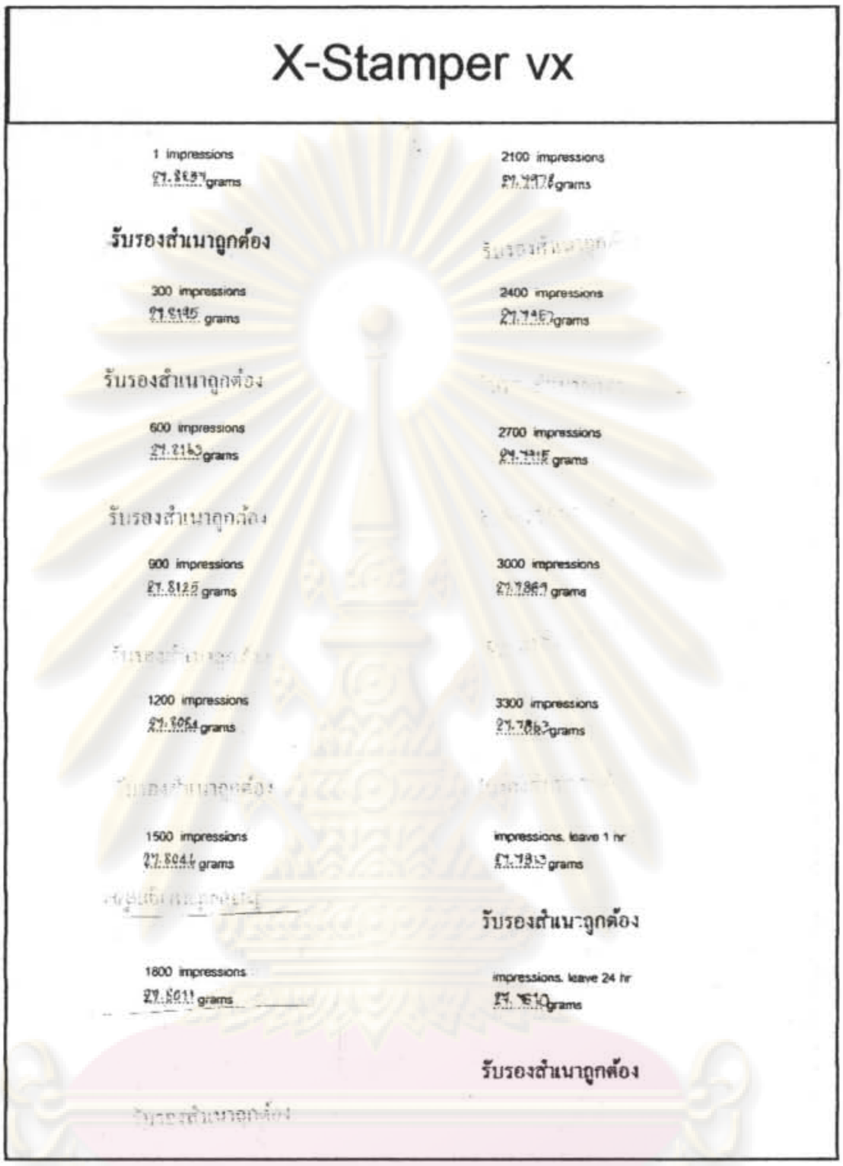


Figure 4.64 Quality of imprints and number of imprints of X-stamper vx.

The result indicated that NaCl- mixed Emanon formula 9 gave the best quality of imprints. The comparison result imprint of formula 9 with pre-ink stamp X-stamper vx brand showed that sponge rubber from formula 9 offers the highest imprint quality. The test results suggested that $NaNO_3$-100; formula 5 shown in Table A.4 and Emanon-NaCl; formula 9 shown in Table A.3 have the optimal properties of the pre ink.

4.6 Compound cost

The cost of the rubber compound is an important factor for investment, to make the decision of production. Cost of the rubber compound sample was calculated on the basis of 10.5 g per peice. The costs of rubber compounds are compared in Figure 4.65. Formula 1 (1000 phr NaCl) and 2 (800 phr NaCl) were NaCl-rubber compound and formula 10 (700 phr NaCl) and 11 (600 phr NaCl) were NaCl mixed surfactant rubber compound.

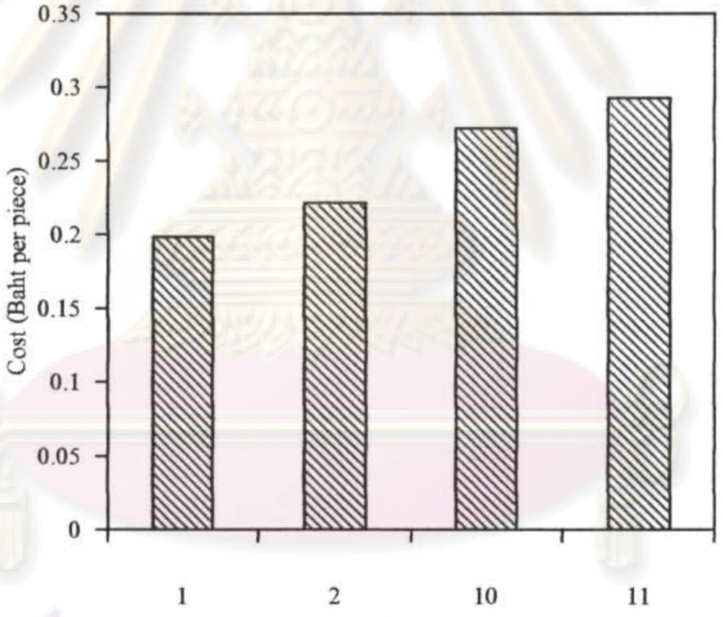


Figure 4.65 Cost of rubber compounds, calculated at 10.5 grams per piece.

The cost decreased with increasing sodium salt content, but increased with increasing of surfactants. For the compounds filled with various carbon black contents and types, costs were not different. The sodium chloride gave cost cheaper than sodium nitrate compound 0.34 baht per piece by average.

Sodium chloride is the most commonly used to form numerous open cell because of low cost and its easy encountered in Thailand. However sodium chloride is also very corrosive, whereas sodium nitrate is much less corrosive [22]. Cost per impression is lower when comparing the cost of stamp, pad, refill ink, stamp racks, and labor. The results have suggested that $NaNO_3$ formula 5 and Emanon-NaCl formula 9 represent the optimal properties of the pre ink at the production cost of THB 0.58 and THB 0.27 respectively.

Using a pre-inked stamp is similar to using an ordinary rubber stamp except that there is no need for a stamp pad. Its main advantages are ease of use and much better print quality. From an economic point of view, the pre-inked stamp has a lower product life cycle cost than a regular rubber stamp even though the unit price of the pre-ink stamp is higher. The cost pre ink stamp from China is 18.51 baht per piece (0.55 US$), 31.35 baht per piece (0.95 US$) for product of Taiwan. Sponge rubber of this research has the total price about 5.27 baht per piece (NaCl-Emanon).

4.7 Formula suitable for pre ink stamp

In Figure 4.66, properties of rubber vulcanizates and sponge rubber by salt leaching method were shown for selection of suitable formula. The best formula to further use in commercial production is NaCl-mixed surfactant Emanon formula 9. In addition, $NaNO_3$ formula 5 is also considered.

Property of rubber	1	2	3	4	5	6	7	8	9	10	11
NaCl and NaCl-surfactant rubber vulcanizate											
Cure property	-	VG	VG	VG	VG	VG	P	G	G	G	G
Salt removal	-	VL	L	P	L	F	VG	VG	VG	VG	VG
Character surface of pre ink stamp	-	VG	VG	VG	VG	VG	G	G	VG	G	G
NaCl and NaCl-surfactant sponge rubber											
Adsorption weight of oil ink	-	X	X	X	X	X	E	VG	E	E	VG
Adsorption time of oil ink	-	X	X	X	X	X	G	G	VG	G	VG
Impression	-	X	X	X	X	X	G	G	E	G	G
$NaNO_3$ and $NaNO_3$-surfactant rubber vulcanizate											
Cure property	F	F	F	F	F	G	VG	P			
Salt removal	G	G	G	G	VG	X	X	VG			
Character surface of pre ink stamp	VG	VG	VG	VG	VG	X	X	P			
$NaNO_3$ and $NaNO_3$-surfactant sponge rubber											
Adsorption weight of oil ink	G	VL	G	VL	VG	X	X	E			
Adsorption time of oil ink	F	X	P	X	F	X	X	VG			
Impression	G	X	G	X	E	X	X	P			

E = Excellent   VG = Very Good   G = Good   F = Fair   P = Pool   L = Low   VL = Very Low

X = Can not salt leaching and can not form character surface   - = can not compound

Figure 4.66 Summary of properties of rubber vulcanizates and sponge rubber by salt leaching method.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Improvement of a sponge rubber production comprised of incorporating fine powder of soluble salts: sodium chloride or sodium nitrate, in the NBR rubber. Rubber with 40% nitrile was compounded in an internal mixer (Brabender Plasticoder) with other ingredients, mixed with sodium salt (sodium chloride or sodium nitrate) and vulcanization systems for vulcanized rubber compounds. The vulcanization systems can be divided into two recipes. The first recipe (Recipe1) including zinc active, stearic acid, MBTS, DPG, sulfur and NaCl or $NaNO_3$. The second recipe (Recipe2) consisting of zinc oxide, stearic acid, MBTS, DPG, sulfur, NaCl or $NaNO_3$ as well as surfactant. In this study, various parameters were studied in semi-efficient vulcanization system. After rubbers were cured, remove salts by washing in water or methanol in case salt combined surfactant and then dried.

Parameters influenced the property of the sponge rubbers determined in this study are as follow: particle size of salts (100, 300 and 400 mesh), content of water-soluble salts (600, 700, 800 and 1000 phr), type of carbon black (N-220, N-330 and N-774) and their amount (20 and 50 phr), type of surfactant (nonionic; Emanon3299R and anionic; Neopelex F-50 and Emal 270TH). The mechanical, physical properties and characteristics of the compound rubbers were studied by moving die rheometer, hardness shore C and scanning electron microscope. The removal time of sodium salts were also investigated. The pre-ink stamp is used for checking of imprints. The costs of the production prepared by this method was also reported. The results are summarized as follows:

1) For the rheomatric characteristics of the various blends, cure time (tc_{90}) for the rubber with NaCl is shorter than that of $NaNO_3$. Sodium chloride was combined with surfactant (Emanon), as formula 9; Emanon, its recipe was the most suitable. Both hot press process and removal salt process because of formula 5 of $NaNO_3$ systems had cure time (tc_{90}) higher than formula 9; Emanon and at the same time of removing salt, % removal weight of $NaNO_3$ formula 5 lesser than formula 9; Emanon.

2) The percentage of removing of salt depends on particle size and content of salts. The salt with large particle size can be easily removed. The best result in removing salt appears in non-ionic surfactant system, Emanon.

3) A porous rubber stamp material having a spring hardness shore C of 5-10 IRHD in case sodium salt combined with surfactant were prepared. The compound are not combined surfactant, the sponge rubber have a spring hardness 11-28. The harness property depend on carbon black types and content, particle size of salts and contents.

4) From microscopic studies, open cells cannot be formed in rubber containing NaCl. On the other hand, open cell can be formed in rubber containing $NaNO_3$ but the interconnection of pore is not very good.

Pore sizes 50-100 and 5-50 microns were found in sponge rubber from $NaNO_3$ with 100 and 300 mesh, respectively

5) The sponge rubber from NaCl-Emanon (formula 9) and $NaNO_3$ (formula 5) gave the best result in impression test. But $NaNO_3$ formula 5 required inking time more than NaCl-Emanon formula 9.

5.2 Future work

In the field of sponge rubbers, further study should be focused on using soluble starch without surfactant in order to improve interconnection of open cells.

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APPENDICES

APPENDIX A

FORMULATION OF SPONGE RUBBERS

Table A.1 Code of sponge rubber in each compound filled with NaCl and NaCl-surfactant

1	50C330 1000Cl-300	**4**	20C220 800Cl-300	**7**	60C774 800Cl-400 Neopelex	**10**	60C774 700Cl-400 Emal
2	50C330 800Cl-300	**5**	20C220 600Cl-300	**8**	60C774 800Cl-400 Emal	**11**	60C774 600Cl-400 Emal
3	50C220 800Cl-300	**6**	20C220 800Cl-100	**9**	60C774 800Cl-400 Emanon		

Table A.2 Code of sponge rubber in each compound filled with $NaNO_3$ and $NaNO_3$-surfactant

1	50C330 800 NO_3-300	**3**	20C220 800 NO_3-300	**5**	20C220 800NO_3-100	**7**	60C774 800 NO_3-400 Emal 270TH
2	50C220 800 NO_3-300	**4**	20C220 600 NO_3-300	**6**	60C774 800 NO_3-400 Neopelex	**8**	60C774 800 NO_3-400 Emanon

Table A.3 Compositions of sponge rubber in each compound filled with NaCl and NaCl- surfactant

Ingredient	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
N-220	-	-	50	20	20	20	-	-	-	-	-
N-330	50	50	-	-	-	-	-	-	-	-	-
N-774	-	-	-	-	-	-	60	60	60	60	60
RALOX	2	2	2	2	2	2	2	2	2	2	2
NaCl 100mesh	-	-	-	-	-	800	-	-	-	-	-
NaCl 300 mesh	1000	800	800	800	600	-	-	-	-	-	-
NaCl 400 mesh	-	-	-	-	-	-	800	800	800	700	600
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Neopelex	-	-	-	-	-	-	120	-	-	-	-
EMAL	-	-	-	-	-	-	-	120	-	120	120
EMANON	-	-	-	-	-	-	-	-	120	-	-
NBR ACN 40	100	100	100	100	100	100	100	100	100	100	100
DOP	30	30	30	30	30	30	30	30	30	30	30
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
MBTS	1	1	1	1	1	1	1	1	1	1	1
DPG	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

Table A.4 Compositions of sponge rubber in each compound filled with $NaNO_3$ and $NaNO_3$- surfactant

Ingredient	1	2	3	4	5	6	7	8	9	10
N-220	-	50	20	20	20	-	-	-	-	-
N-330	50	-	-	-	-	-	-	-	-	-
N-774	-	-	-	-	-	60	60	60	60	60
RALOX	2	2	2	2	2	2	2	2	2	2
$NaNO_3$ 100mesh	-	-	-	-	800	-	-	-	-	-
$NaNO_3$ 300 mesh	800	800	800	600	-	-	-	-	-	-
Na $NO_3$400 mesh	-	-	-	-	-	800	800	800	700	600
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Neopelex	-	-	-	-	-	120	-	-	-	-
Emal	-	-	-	-	-	-	120	-	120	120
Emanon	-	-	-	-	-	-	-	120	-	-
NBR ACN 40	100	100	100	100	100	100	100	100	100	100
DOP	30	30	30	30	30	30	30	30	30	30
ZnO	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
MBTS	1	1	1	1	1	1	1	1	1	1
DPG	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

APPENDIX B

CURE CURVES OF COMPOUNDS FROM RHEOMETER TEST

Table B.1 Minimum torque of NBR compounds, sulfur curing at 1.5 phr

NaCl

No.	(2) 50C330 800Cl-300	(3) 50C220 800Cl-300	(4) 20C220 800Cl-300	(5) 20C220 600Cl-300	(6) 20C330 800Cl-100
1	10.95	17.12	12.51	5.31	18.58
2	13.54	19.12	12.00	4.31	19.63
Med.	12.45	18.12	12.25	4.8	19.2
SD.	1.83	1.41	0.36	1.41	1.83

NaCl-Surfactant

No.	(7) 60C774 800Cl-400 Neopelex	(8) 60C774 800Cl-400 Emal	(9) 60C774 800Cl-400 Emanon	(10) 60C774 700Cl-400 Emal	(11) 60C774 600Cl-400 Emal
1	5.00	19.76	4.80	4.57	1.71
2	-	-	-	-	-
Med.	5.00	19.76	4.80	4.57	1.71
SD.	-	-	-	-	-

$NaNO_3$

No.	(1) 50C330 800NO3-300	(2) 50C220 800NO3-300	(3) 20C220 800NO3-300	(4) 20C220 600NO3-300	(5) 20C220 800NO3-100
1	6.78	8.31	6.05	5.03	7.92
2	7.52	6.07	5.83	3.70	8.96
Med.	7.15	7.19	5.94	4.36	8.44
SD.	0.52	1.58	0.15	0.94	0.73

$NaNO_3$-Surfactant

No.	(6) 60C774 800NO3-400 Neopelex	(7) 60C774 800NO3-400 Emal	(8) 60C774 800NO3-400 Emanon
1	0.65	1.85	0.58
2	-	-	0.60
Med.	0.65	1.85	0.59
SD.	-	-	0.01

Table B.2 Maximum torque of NBR compounds, sulfur curing at 1.5 phr

NaCl

No.	(2) 50C330 800Cl-300	(3) 50C220 800Cl-300	(4) 20C220 800Cl-300	(5) 20C220 600Cl-300	(6) 20C330 800Cl-100
1	17.40	31.45	26.93	20.54	31.58
2	20.52	34.98	28.04	17.82	29.68
Med.	18.96	33.21	27.48	19.18	30.63
SD.	2.20	2.49	0.78	1.92	1.34

NaCl-Surfactant

No.	(7) 60C774 800Cl-400 Neopelex	(8) 60C774 800Cl-400 Emal	(9) 60C774 800Cl-400 Emanon	(10) 60C774 700Cl-400 Emal	(11) 60C774 600Cl-400 Emal
1	11.58	25.35	20.89	19.78	19.48
2	-	-	-	-	-
Med.	11.58	25.35	20.89	19.78	19.48
SD.	-	-	-	-	-

$NaNO_3$

No.	(1) 50C330 800NO3-300	(2) 50C220 800NO3-300	(3) 20C220 800NO3-300	(4) 20C220 600NO3-300	(5) 20C220 800NO3-100
1	18.87	32.24	23.09	23.64	15.26
2	18.46	24.75	22.43	22.49	14.44
Med.	18.66	28.49	22.76	23.06	14.85
SD.	0.28	5.29	0.46	0.81	0.57

$NaNO_3$-Surfactant

No.	(6) 60C774 800NO3-400 Neopelex	(7) 60C774 800NO3-400 Emal	(8) 60C774 800NO3-400 Emanon
1	1.64	3.80	9.16
2	-	-	9.24
Med.	1.64	3.80	9.20
SD.	-	-	0.17

Table B.3 Scorch time of NBR compounds, sulfur curing at 1.5 phr

NaCl

No.	(2) 50C330 800Cl-300	(3) 50C220 800Cl-300	(4) 20C220 800Cl-300	(5) 20C220 600Cl-300	(6) 20C330 800Cl-100
1	2.75	1.19	1.71	1.75	2.14
2	2.38	1.20	1.68	1.71	2.43
Med.	2.56	1.19	1.69	1.73	2.28
SD.	0.26	0.01	0.02	0.02	0.20

NaCl-Surfactant

No.	(7) 60C774 800Cl-400 Neopelex	(8) 60C774 800Cl-400 Emal	(9) 60C774 800Cl-400 Emanon	(10) 60C774 700Cl-400 Emal	(11) 60C774 600Cl-400 Emal
1	9.40	4.49	2.74	3.02	3.31
2	-	-	-	-	-
Med.	9.40	4.49	2.74	3.02	3.31
SD.	-	-	-	-	-

$NaNO_3$

No.	(1) 50C330 800NO3-300	(2) 50C220 800NO3-300	(3) 20C220 800NO3-300	(4) 20C220 600NO3-300	(5) 20C220 800NO3-100
1	1.81	1.89	1.85	1.49	2.75
2	1.79	2.03	1.86	1.52	3.19
Med.	1.80	1.96	1.85	1.50	2.97
SD.	0.01	0.09	0.01	0.02	0.31

$NaNO_3$-Surfactant

No.	(6) 60C774 800NO3-400 Neopelex	(7) 60C774 800NO3-400 Emal	(8) 60C774 800NO3-400 Emanon
1	8.50	2.31	9.63
2	-	-	-
Med.	8.50	2.31	9.63
SD.	-	-	-

Table B.4 Cure time of NBR compounds, sulfur curing at 1.5 phr

NaCl

No.	**(2) 50C330 800Cl-300**	**(3) 50C220 800Cl-300**	**(4) 20C220 800Cl-300**	**(5) 50C220 800Cl-300**	**(6) 50C330 800Cl-300**
1	6.82	4.86	4.29	4.48	8.02
2	5.75	6.50	3.90	6.57	6.03
Med.	6.28	5.68	4.09	5.52	7.02
SD.	0.75	1.15	0.27	1.47	1.40

NaCl-Surfactant

No.	**(7) 60C774 800Cl-400 Neopelex**	**(8) 60C774 800Cl-400 Emal**	**(9) 60C774 800Cl-400 Emanon**	**(10) 60C774 700Cl-400 Emal**	**(11) 60C774 600Cl-400 Emal**
1	62.50	22.94	22.14	15.05	23.70
2	-	-	-	-	-
Med.	62.50	22.94	22.14	15.05	23.70
SD.	-	-	-	-	-

$NaNO_3$

No.	**(1) 50C330 800NO3-300**	**(2) 50C220 800NO3-300**	**(3) 20C220 800NO3-300**	**(4) 20C220 600NO3-300**	**(5) 20C220 800NO3-100**
1	29.38	33.50	33.44	43.54	37.55
2	30.77	30.81	36.36	40.87	37.89
Med.	30.07	32.15	34.90	42.20	37.72
SD.	0.98	1.90	2.06	1.88	0.24

$NaNO_3$-Surfactant

No.	**(6) 60C774 800NO3-400 Neopelex**	**(7) 60C774 800NO3-400 Emal**	**(8) 60C774 800NO3-400 Emanon**
1	21.39	4.21	62.34
2	-	-	64.50
Med.	21.39	4.21	63.42
SD.	-	-	1.52

Table B.5 Removal weight of character surface sodium chloride were washed out for three, ten and fifteen hours in the ultrasonic cleaner at 60°C and then dried at 40°C in an oven.

Compounds	Weight before washing (gram)	Weight after washing 3 hrs. (gram)	% removal weight	Weight after washing 10 hrs. (gram)	% removal weight	Weight after washing 15 hrs. (gram)	% removal weight
(2) 50C330 800Cl-300	10.8541	9.1307	15.88	5.1669	52.40	3.8847	64.21
(3) 50C220 800Cl-300	10.5984	9.1061	14.08	5.6739	46.46	3.8773	63.42
(4) 20C220 800Cl-300	10.6071	8.6966	18.01	4.3025	59.44	2.7128	74.42
(5) 20C220 600Cl-300	10.1640	8.5092	16.28	4.7033	53.73	3.4116	66.43
(6) 20C220 800Cl-100	10.9817	8.5930	21.75	3.0990	71.78	1.8889	79.80
30C220 800Cl-100	10.6324	8.3776	21.21	3.1914	69.98	2.7704	73.94
35C220 800Cl-100	10.6091	8.2436	22.30	2.8031	73.58	2.3887	77.48
40C330 800Cl-300	10.2131	9.0381	11.50	6.3359	37.96	5.8199	43.02
45C330 800Cl-300	10.9301	9.2114	15.72	5.2586	51.89	3.6561	66.55

Table B.6 Removal weight of character surface sodium chloride-surfactant were washed out for three hours in the ultrasonic cleaner at 60°C and then dried at 40°C in an oven.

Compounds	**Weight before washing (gram)**	**Weight after washing 3 hrs. (gram)**	**% removal weight**
(7) 60C774 800Cl-400 Neopelex F-50	9.8566	1.8640	81.09
(8) 60C774 800Cl-400 Emal 270TH	9.4361	1.9369	79.47
(9) 60C774 800Cl-400 Emanon	8.9956	1.6809	81.31
(10) 60C774 700Cl-400 Emal 270TH	8.9864	2.0602	77.07
(11) 60C774 600Cl-400 Emal 270TH	8.8210	1.8239	79.32

Table B.7 Removal weight of character surface sodium nitrate was immersed in methanol for ½ hour, removal of the surfactant and sodium nitrate was carried out with water using ultrasonic cleaner, at 60°C for 3 and 5 hours, then dried at 40°C in an oven.

Compounds	Weight before washing	Weight after washing 3 hrs. (gram)	% removal	Weight after washing 5 hrs. (gram)	% removal
20C220 800NO$_3$-100	10.31536	2.1752	78.91	1.9287	81.30
20C220 600 NO$_3$-300	9.791644	3.3508	65.78	2.2628	76.89
20C220 800 NO$_3$-300	9.986378	3.0421	69.54	1.9732	80.24
50C220 800 NO$_3$-300	10.15499	3.1911	68.58	2.4829	75.55
50C330 800 NO$_3$-300	10.40153	3.2910	68.36	2.1259	79.56
60C774 800 NO$_3$-400 Neopelex F-50	N/A	N/A	N/A	N/A	N/A
60C774 800 NO$_3$-400 Emal 270TH	N/A	N/A	N/A	N/A	N/A
60C774 800 NO$_3$-400 Emanon	9.0102	1.6778	81.38	-	-

Table B.8 Removal percent weight of smooth surface sodium chloride were washed out for three hours in the ultrasonic cleaner at 60°C and then dried at 40°C in an oven (specimen of SEM testing 0.5x0.5x0.5 cm).

Compounds	Weight before washing	Weight after washing 3 hrs. (gram)	% removal
20C220 800Cl-100	0.4079	0.0715	82.47
30C220 800Cl-100	0.3017	0.0620	79.45
35C220 800Cl-100	0.3658	0.0847	76.85
20C220 600Cl-300	0.3012	0.0842	72.05
20C220 800Cl-300	0.2899	0.0754	73.99
50C220 800Cl-300	0.3197	0.0965	69.82
40C330 800Cl-300	0.3405	0.1017	70.13
45C330 800Cl-300	0.3111	0.1054	66.12
50C330 800Cl-300	0.2959	0.0757	74.42
60C774 800 NO_3-400 Neonelex F-50	0.1437	0.0230	83.99
60C774 800 NO_3-400 Emal 270TH	0.1182	0.0190	83.93
60C774 600 NO_3-400 Emal 270TH	0.1611	0.0308	80.88
60C774 700 NO_3-400 Emal 270TH	0.1417	0.0241	82.99
60C774 800 NO_3-400 Emanon	0.1196	0.0165	86.20

Table B.9 Removal percent weight of smooth surface sodium nitrate were washed out for three hours in the ultrasonic cleaner at 60°C and then dried at 40°C in an oven (specimen of SEM testing 0.5x0.5x0.5 cm).

Compounds	Weight before washing	Weight after washing 3 hrs. (gram)	% removal
20C220 800NO$_3$-100	0.2983	0.0715	82.37
20C220 600 NO$_3$-300	0.2831	0.0842	78.13
20C220 800 NO$_3$-300	0.3018	0.0754	81.68
50C220 800 NO$_3$-300	0.2828	0.0965	80.16
50C330 800 NO$_3$-300	0.2510	0.0757	80.32
60C774 800 NO$_3$-400 Neopelex F-50	N/A	N/A	N/A
60C774 800 NO$_3$-400 Emal 270TH	N/A	N/A	N/A
60C774 800 NO$_3$-400 Emanon	0.1441	0.0236	83.62

Table B.10 Average of Hardness values of filled NaCl form sponge rubber

Compounds	Hardness shore C	SD.
(2) 50C330 800Cl-300	60	0.64
(3) 50C220 800Cl-300	62	0.97
(4) 20C220 800Cl-300	28	0.49
(5) 20C220 600Cl-300	45	0.49
(6) 20C220 800Cl-100	35	0.56
30C220 800Cl-100	45	0.70
35C220 800Cl-100	50	0.81
40C330 800Cl-300	45	0.31
45C330 800Cl-300	65	0.73
(7) 60C774 800Cl-400 Neopelex F-50	7	2.42
(8) 60C774 800Cl-400 Emal 270TH	9	1.06
(9) 60C774 800Cl-400 Emanon	6	3.81
(10) 60C774 700Cl-400 Emal 270TH	10	3.69
(11) 60C774 600Cl-400 Emal 270TH	9	3.59

Table B.11 Average of Hardness values of filled NaNO$_3$ form sponge rubber

Compounds	Hardness shore C	SD.
(2) 50C330 800 NO$_3$-300	25	4.81
(3) 50C220 800 NO$_3$-300	30	3.10
(4) 20C220 800 NO$_3$-300	28	2.57
(5) 20C220 600 NO$_3$-300	42	1.76
(6) 20C220 800NO$_3$-100	11	3.16
(7) 60C774 800 NO$_3$-400 Neopelex F-50	N/A	N/A
(8) 60C774 800 NO$_3$-400 Emal 270TH	N/A	N/A
(9) 60C774 800 NO$_3$-400 Emanon	5	1.47

Table B.12 Weight of oil ink after inking on sponge rubber for 1 h and first time were detected, when ink ooze out on paper. The compound rubber filled sodium chloride with surfactant in the NBR rubber.

Compounds	Weight of sponge before inking	Weight of sponge after inking for 1 hr	Weight of oil ink (grams)	The first time of ink ooze out on paper (minutes)
(7) 60C774 800Cl-400 Neopelex F-50	1.8723	4.4515	2.5792	36
(8) 60C774 800Cl-400 Emal 270TH	1.8271	4.0666	1.8826	35
(9) 60C774 800Cl-400 Emanon	1.6936	4.0227	2.2395	17
(10) 60C774 700Cl-400 Emal 270TH	1.9196	3.8022	2.3291	30
(11) 60C774 600Cl-400 Emal 270TH	2.0547	3.8410	1.7863	22

Table B.13 Weight of oil ink after inking on sponge rubber for 1 h and first time were detected, when ink ooze out on paper. The compound rubber filled sodium nitrate with surfactant in the NBR rubber.

Compounds	Weight of sponge before inking	Weight of sponge after inking for 1 hr	Weight of oil ink (grams)	The first time of ink ooze out on paper (minutes)
(1)50C330 800 NO$_3$-300	2.1620	2.6607	0.4987	95
(2) 50C220 800 NO$_3$-300	2.3353	2.3946	0.0593	N/A
(3) 20C220 800 NO$_3$-300	1.9967	2.4667	0.4700	115
(4) 20C220 600 NO$_3$-300	2.2400	2.2496	0.0096	N/A
(5) 20C220 800NO$_3$-100	2.4066	3.7475	1.3409	72
(8) 60C774 800 NO$_3$-400 Emanon	1.6790	4.0023	2.3233	20

Table B.14 Time average, standard derivation and weight average, standard derivation of impression test per 300 times of sponge rubber form NaCl and surfactants.

Compounds	Time average (minutes)	Weight average (grams)
X-Stamper vx	1.60	0.0036
(7) 60C774 **800Cl-400** **Neopelex F-50**	1.67	0.0136
(8) 60C774 **800Cl-400** **Emal 270TH**	1.67	0.0077
(9) 60C774 **800Cl-400** **Emanon**	1.67	0.0130
(10) 60C774 **700Cl-400** **Emal 270TH**	1.52	0.0054
(11) 60C774 **600Cl-400** **Emal 270TH**	1.50	0.0101

Table B.15 Time average, standard derivation and weight average, standard derivation of impression test per 300 times of sponge rubber form NaNO$_3$ and NaNO$_3$ combined surfactants.

Compounds	Time average (minutes)	Weight average (grams)
(1) 50C330 800 NO$_3$-300	1.59	0.0040
(3) 20C220 800 NO$_3$-300	1.55	0.0027
(5) 20C220 800NO$_3$-100	1.51	0.0079
(8) 60C774 800 NO$_3$-400 Emanon	1.64	0.0050

Table B.16 Cost of sponge rubber in each compound filled NaCl and surfactant

Compounds	Cost		
	Baht/piece	**Baht / kilogram**	**Baht/ square meter**
(1) 50C330 1000Cl-300	0.20	18.89	143.55
(2) 50C330 800Cl-300	0.22	21.17	156.88
(3) 50C220 800Cl-300	0.22	21.08	156.32
(4) 20C220 600Cl-300	0.25	24.08	172.06
(5) 20C220 800Cl-300	0.22	20.91	155.08
(6) 20C220 800Cl-100	0.22	20.74	153.81
30C220 800Cl-100	0.22	20.85	154.63
35C220 800Cl-100	0.22	20.91	155.08
40C330 800Cl-300	0.22	21.06	156.06
45C330 800Cl-300	0.22	21.11	156.48
(7) 60C774 800Cl-400 **Neopelex F-50**	0.26	24.99	169.91
(8) 60C774 800Cl-400 **Emal 270TH**	0.26	24.35	165.55
(9) 60C774 800Cl-400 **Emanon**	0.27	25.63	174.28
(10) 60C774 700Cl-400 **Emal 270TH**	0.27	25.94	172.27
(11) 60C774 600Cl-400 **Emal 270TH**	0.29	27.89	180.71

Table B.17 Cost of sponge rubber in each compound filled $NaNO_3$ and surfactant

Compounds	Cost		
	Baht/piece	Baht / kilogram	Baht/ square meter
(1) 50C330 800 NO_3-300	0.58	55.06	408.12
(2) 50C220 800 NO_3-300	0.572	54.97	407.69
(3) 20C220 800 NO_3-300	0.58	55.33	410.31
(4) 20C220 600 NO_3-300	0.60	57.19	408.54
(5) 20C220 800NO_3-100	0.58	55.69	413.02
(6)60C774 800 NO_3-400 Neopelex F-50	0.58	54.94	373.58
(7) 60C774 800 NO_3-400 Emal 270TH	0.57	54.30	369.21
(8) 60C774 800 NO_3-400 Emanon	0.58	55.58	377.94

APPENDIX C

COST OF SPONGE RUBBERS

Table C.1 Calculated cost of a sponge rubber

	Size of sponge rubber	Weight (g)	Weight (g) + 10% of waste				
	20W*50L*4H(cm)	9.5	10.5				
Item/Process	**Grinding salts**	**Compound rubber**	**Two roll mill**	**Cure characteristic**	**Press**	**Removal salts**	**Inking**
Process cost	-	-	-	0.0697	-	-	-
Labor cost	0.0263	0.0018	0.0012	-	0.56	-	0.0036
Device	0.0151	0.0093	0.0021	-	2.94	0.0338	-
Total	**0.0414**	**0.0111**	**0.0033**	**0.0697**	**3.50**	**0.0338**	**0.0036**
Time of used	48 hr	15 min	10 min	1-2 day	13 min/12 peice	3 hr	30 min
				Cost production of pre-ink stamp rubber			
				Cost	Size of sponge rubber 20W*50L*4H		
				Production cost (฿/pcs.)	3.66	R/M methanol cost	1.61
				R/M (฿/pcs.)	0.28	R/M oil ink	18.00
				Total cost (฿/piece)		23.55	

VITAE

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