CHAPTER IV

RESULTS AND DISCUSSION

In this study, the solder mask from natural rubber latex was prepared by using the prevulcanization of concentrated latex with the additives and by adjusting the viscosity by a thickening agent.

The goals of this research were to obtain the optimum method and ingredients for the preparation of solder mask by varying the time for prevulcanization and the concentration of stabilizers, vulcanizing system, filler, and thickening agents. Finally, the physical and mechanical properties of the solder masks were investigated to determine the optimum concentration of ingredients that gives suitable properties.

4.1 Properties of Raw Materials

4.1.1 Natural Rubber latex

The natural rubber latex concentrate or concentrated latex consists of particles of rubber hydrocarbon and non-rubber constituents suspended in an aqueous serum phase. The range of dry rubber content is between 60.0-61.0%.

The properties test results of natural rubber latex, used in this study, are shown in Table 4.1. The average particle diameter of natural rubber latex is shown in Table

4.2 and the particle size distribution was determined by the mastersizer shown in Appendix A.

Table 4.1 The properties test results of natural rubber latex

Type of latex : High Ammonia

Date of production : 12/02/99   Date of test : 12/02/99

Properties	Test results
Total Solids Content, %	62.65
Dry Rubber Content, %	61.20
Non Rubber Solids, %	1.45
Ammonia Content (on Total Weight), %	0.67
Ammonia Content (on Water Phase), %	1.79
pH Value	10.60
KOH Number	0.48
Volatile Fatty Acid Number (V.F.A.)	0.0155
Mechanical Stability Time @ 55% TS., Sec	60 (12-02-99)
Specific Gravity at 25 °C	-
Magnesium Content (ppm.)	25

Source : Revertex (Thailand) Ltd., Bangplee Samutprakarm.

4.1.2 Zinc Oxide (ZnO), Tetramethyl Thiuram Disulfide (TMTD), Zinc Dibutyl Dithiocarbamate (ZBDC), Titanium Dioxide Dispersion (TiO_2)

The average particle diameters of ingredient dispersions are shown in Table 4.2 and the particle size distributions were determined by the mastersizer as shown in Appendix A.

Table 4.2 The average particle diameters of natural rubber latex and ingredient dispersions

Dispersions	Average particle diameter (μm.)
Natural Rubber Latex	0.773
50% ZnO	0.393
50% TMTD	5.323
33% ZBDC	1.870
50% TiO_2	0.260

In this research, all of compounding ingredients were added to natural rubber latex as aqueous solution dispersions or emulsions. The stability of dispersions and emulsions would be comparable to that of the natural rubber latex which they were added to. Ingredient dispersions were prepared by ball mill because the particle sizes of the powder ingredients were larger than natural rubber latex. If the powder ingredients were mixed directly into the concentrated latex, they would precipitate within the short time. Therefore, the ingredient dispersions were prepared by ball mill to produce dispersions of small particle to approach the natural rubber latex that is shown in Table 4.2.

4.2 Preparation of Prevulcanized Latex

In this experiment, prevulcanized latex was prepared in a thiuram vulcanization system that was supplied by the reaction between tetramethyl thiuram disulfide and zinc oxide. The additives consisted of tetramethyl thiuram disulfide (TMTD), zinc dibutyl dithiocarbamate (ZBDC), zinc oxide (ZnO), thiourea and titanium dioxide (TiO_2). They acted as the vulcanizing agent, accelerator, accelerator activator and filler, respectively. Vulcanization by TMTD and ZnO, at a temperature as low as 100°C, is a slow process but thiourea is able to activate vulcanization. The optimum ratio of thiourea to TMTD corresponds to a mole ratio of approximately 1:1. The stabilized compositions during prevulcanization comprise potassium hydroxide (KOH), tergitol NP9 and casein, which acted as the pH adjuster, surfactant and protective colloid. The thiuram vulcanizates have excellent heat and aging resistance.

According to the required degree of vulcanization, it is preferable to allow the prevulcanized latex to mature for a period of about 7 days at room temperature. During this time, certain changes take place in the latex. The consequences are an initial drop in the tensile strength of dried films, followed by a gradual increase. Little further change occurs after about 7 days, even during prolonged storage. The advantages that accrue from this period of maturation may be summed up as improved uniformity, both of behaviors during subsequent processing and of the properties of the finished product.

4.2.1 Effect of Prevulcanization Time to Degree on Vulcanization

The solder masks were prepared from compounded latex without heat, the long drying time was required. So the compounded latex would be prevulcanized to decrease drying time. The formulation of compounded latices were obtained as follows:

- 60% Natural rubber latex	100	Parts by dry weight
- 15% Casein	0.5	phr
- 25% Tergitol NP 9	0.5	phr
- 10% KOH	0.75	phr
- 50% ZnO	1	phr
- 50% TMTD	3	phr
- 33% ZBDC	1	phr
- 10% Thiuram	1	phr
- 50% Titanium dioxide	2.5	phr

Prevulcanized latex is very similar in appearance to unvulcanized latex. The original fluidity is retained, although the vulcanized product tends to be slightly yellow. The degree of vulcanization of the prevulcanized latex was determined by chloroform test. It was a simple procedure for ascertaining the extent of cure. A small volume of latex was mixed with an equal volume (10 ml.) of chloroform (or carbon tetrachloride) until coagulation occurs. The physical state of the coagulum, which is produced, gives an indication of the state of cure of prevulcanized latex. At least four distinct stages may be distinguished. Characteristic of rubber latex coagulation showed the degree of vulcanization[9]:

Degree of vulcanization	Characteristic of rubber latex coagulation
No.1 (Unvulcanized)	One sticky coagulum and extensible
No.2 (Lightly vulcanized)	Soft and rough piece
No.3 (Moderately vulcanized)	Crumbly and non-sticky seeds
No.4 (Fully vulcanized)	Dry and friable coagulum

Compounded latex was heated at 70-80°C for 0, 2, 4 and 6 hours, degrees of vulcanization are shown in Table 4.3.

Table 4.3 Degree of vulcanization of prevulcanized latex at various times for prevulcanization

Prevulcanization time	Degree of vulcanization
0	No.1
2	No.1^+
4	No.2-2^+
6	No.3-3^+

+ The appearance is in between the states of the number indicated and the higher degree of vulcanization.

From the Table 4.3, the degree of vulcanization increased with increasing prevulcanization time. At a prevulcanization time of 2 hours, the prevulcanized latex had a degree of vulcanization No.1$^+$. It has the physical state of rubber coagulum between No.1 and No.2. Similarly, the degree of vulcanization No.2$^+$ and No.3$^+$ have the physical state of rubber coagulum between No.2-3 and No.3-4, respectively. The solder masks were prepared from prevulcanized latex at a degree of vulcanization No.1-2$^+$. They had a long drying time of approximately 30-45 minutes at 80°C. A drying time about 20 minutes was required for the prevulcanized latex at a degree of vulcanization No.3-3$^+$. At degree of vulcanization No.4 for preparing solder masks, the solder mask films were ruptured. Therefore, the appropriate prevulcanization time of 6 hours was used because they could be dried in a short time and the solder mask films were not ruptured.

4.2.2 Effect of KOH Concentration

The compounded latex was coagulated during prevulcanization or after mixing with viscosity modifier if no stabilizers was in the compound latex. In this study, the stabilizer comprised of KOH, tergitol NP9 and casein that acted as the pH adjuster, surfactant and protective colloids, respectively.

The effect of KOH concentration on the stability of prevulcanized latex was studied by varying the KOH concentrations to 0.25, 0.5, 0.75 and 1 phr. The stability of prevulcanized latex was reported in mechanical stability time (MST). The natural rubber latice mechanical stability apparatus is shown in Appendix B.

The mechanical stability time of prevulcanized latices at various KOH concentrations are shown in Table 4.4.

Table 4.4 Mechanical stability time (MST) of prevulcanized latex at various amounts of KOH

Amount of KOH (phr)	MST (seconds)
0.25	93
0.5	83
0.75	100
1	118

As can be seen in Table 4.4, the MST of prevulcanized latex decreased with increasing KOH concentration from 0.25 to 0.5 phr and the MST increased with increasing KOH concentration from 0.5 to 1 phr. Anions from KOH are thought to be adsorbed on the surfaces of the rubber particles, possibly partial displacing adsorbed proteins. They then interact with metallic ions, such as those of calcium and magnesium, which are present in the latex initially. The process of coagulation may be accelerated by the addition of small amount of KOH and the addition of larger amount, which causes a retardation of MST. The range of KOH addition depends upon the amount of calcium and magnesium ions, which are present in the latex. The appropriate KOH concentration of 1 phr was used because it gave the best MST.

4.2.3 Effect of Surfactant Concentration

The first additive, the surfactant, was mixed with the latex to improve stability. The effect of surfactant concentration on MST of prevulcanized latex was studied by varying the tergitol NP 9 concentrations to 0.25, 0.5, 0.75 and 1 phr. A

KOH concentration of 1 phr was used. Other ingredients as shown in the formulation were used to determine the appropriate prevulcanization time. The MST of prevulcanized latex at various tergitol NP 9 concentrations is shown in Table 4.5.

Table 4.5 MST of prevulcanized latex at various amounts of tergitol NP 9

Amount of tergitol NP 9 (phr)	MST (seconds)
0.25	95
0.5	118
0.75	59
1	48

From Table 4.5, the best MST of the prevulcanized latex occurred when 0.5 phr of tergitol NP 9 was used. Typical ranges of surfactant were 0.2-0.4 phr[11]. Increasing the amounts of tergitol NP 9 above 0.5 phr tended to decrease the MST of prevulcanized latex. The addition tergitol NP 9 was over 1 phr; the latex was coagulated during prevulcanization. Therefore, the appropriate tergitol NP 9 concentration of 0.5 phr was used.

4.2.4 Effect of Protective Colloid Concentration

Casein was used in this study. It is a phosphoprotein, which is obtained from casenogen, the raw protein of milk. The effect of the protective colloid concentration on the MST of prevulcanized latex was studied by varying the amounts of casein to

0.25, 0.5 and 0.75 phr. The KOH and tergitol NP9 concentrations were used at 1 and 0.5 phr, respectively. Other ingredients as shown in the formulation were used to determine the appropriate prevulcanization time. The MST of prevulcanized latex at various casein concentrations is shown in Table 4.6.

Table 4.6 MST of prevulcanized latex at various amounts of casein

Amount of casein (phr)	MST (seconds)
0.25	100
0.5	118
0.75	161

As shown in Table 4.6, the MST of prevulcanized latex increased with increasing amounts of casein. The protective colloids also function as dispersion and emulsion stabilizers and are sometimes added to disperse systems in order to enhance the colloid stability. The increasing the amounts of casein tends to retard the coagulation of rubber particles in the mechanical stability time test. An appropriate casein concentration of 0.75 phr was used.

4.2.5 Effect of Type of Surfactant

As type of surfactant affected on MST. Tergitol NP9 was replaced by ammonium laurate. At KOH and casein concentrations of 1 and 0.75 phr, ammonium laurate was used by changing the concentrations to 0.05, 0.1 and 0.15 phr. Other ingredients as shown in the formulation were used to determine the appropriate prevulcanization time. The MST of prevulcanized latex at various ammonium laurate concentrations is shown in Table 4.7.

Table 4.7 MST of prevulcanized latex at various amounts of ammonium laurate

Amount of ammonium laurate (phr)	MST (seconds)
0.05	538
0.1	686
0.15	723

From Table 4.7, the MST of prevulcanized latex increased with increasing ammonium laurate concentration and the best MST occurred when 0.15 phr of ammonium laurate was used. The comparison of MST of prevulcanized latex between that prepared from tergitol NP9 and ammonium laurate showed that the MST of prevulcanized latex from tergitol NP9 was less than ammonium laurate. This was because tergitol NP9 is the polyethylene oxide condensate and its stabilizing propensity is lost at elevated temperatures. From ASTM D 1076 and ISO 2004, the standard MST of concentrated latex for at least 650 seconds and for rubber industry MST of latex, should be above 700 seconds. Therefore, the appropriate ammonium laurate concentration of 0.15 phr was used.

4.3 Effect of Vulcanizing Agent

In this study, TMTD was used as the vulcanizing agent because of the fact that a vulcanizate of good heat resistance is suitable for preparing solder mask. The effects of the amount of vulcanizing system on the properties of vulcanized rubber were studied by varying the amounts of TMTD to 1, 2 and 3 phr. The amounts of ZBDC and ZnO, which are acted as the accelerator and accelerator activator of TMTD, were varied in correspondence to the optimum ratio of TMTD. Thiourea can activate the vulcanization of TMTD at a temperature of as low as 100 °C by the optimum mole ratio of approximately 1:1 with TMTD. The formulations of prevulcanized latex were obtained as follows:

60% Natural rubber latex		100	phr
15% Casein		0.75	phr
10% KOH		1	phr
Surfactant	Tergitol NP9,	0.5	phr
	Ammonium laurate	0.15	phr
Vulcanizing system			
50% ZnO		0.33, 0.66, 1.00	phr
50% TMTD		1, 2, 3	phr
33% ZDBC		0.33, 0.66, 1.00	phr
10% Thiourea		0.33, 0.66, 1.00	phr
Filler: 50% Titanium dioxide		2.5	phr

The mechanical properties of the vulcanized sheets and physical property of the solder mask were studied to obtain the appropriate amount of vulcanizing system by comparing tergitol NP9 and ammonium laurate, which both served as the surfactant. The mechanical properties, which were determined in this study, were the tensile strength, the elongation and the hardness. The physical property of solder mask that determined in this study was the adhesion strength in shear.

Tables 4.8, 4.9 and Figures 4.1, 4.2 illustrate the effect of the amount of vulcanizing system and type of surfactant on the mechanical properties. Tensile strength and hardness increased with the increasing amount of vulcanizing system and the elongation at break decreased with the increasing the amount of vulcanizing system.

Table 4.10 and Figure 4.3 illustrate the effect of the amounts of vulcanizing system and type of surfactant on the adhesion strength of solder mask. The adhesion strength decreased with the increasing the amount of vulcanizing system. From the *secondary valence bond theory*, the coherence of films from prevulcanized latex derives mainly from the totality of secondary valence bonds between two molecules of adjacent particles. If the particle is 1μ in diameter, and the primary molecular weight of the rubber hydrocarbon molecule is taken as 300,000, then the particles contain about 10^6 primary rubber molecule. These will be arranged in a tangled, haphazard fashion. Prevulcanization at a high amount of TMTD could produce high crosslinks of rubber molecules. Few rubber molecules remain to be attached with the surface of PCB. When comparing the adhesion strength of solder mask, which used ammonium laurate and tergitol NP9, it was found that the adhesion strength of solder mask that used ammonium laurate had higher values than those that used tergitol NP9.

The tensile strength and elongation of a film obtained from the composition of T.Maeda et al. invention [17] were 50-150 kgf/cm^2 (5.22-15.66 MPa) and 100-800%, respectively. The tensile strength and elongation of vulcanized sheets containing TMTD 2 phr had good values in this range. The adhesion strength of solder mask containing TMTD 2 phr was sufficient enough to prevent ingress of soldering material, but also low enough to allow easy stripping by hand. Therefore, the appropriate amount of vulcanizing system was TMTD 2 phr which an optimum ratio of ZDBC, ZnO and thiourea.

Table 4.8 Effect of the amount of vulcanizing system at ammonium laurate 0.15 phr on the mechanical properties

Properties	Test methods	Amount of TMTD (phr)		
		1	2	3
Tensile strength (MPa)	ISO 37	8.74	14.87	20.89
Elongation at break (%)	ISO 37	886	796	749
Hardness (shore A)	ASTM D 2240	27.6	29.4	31.0

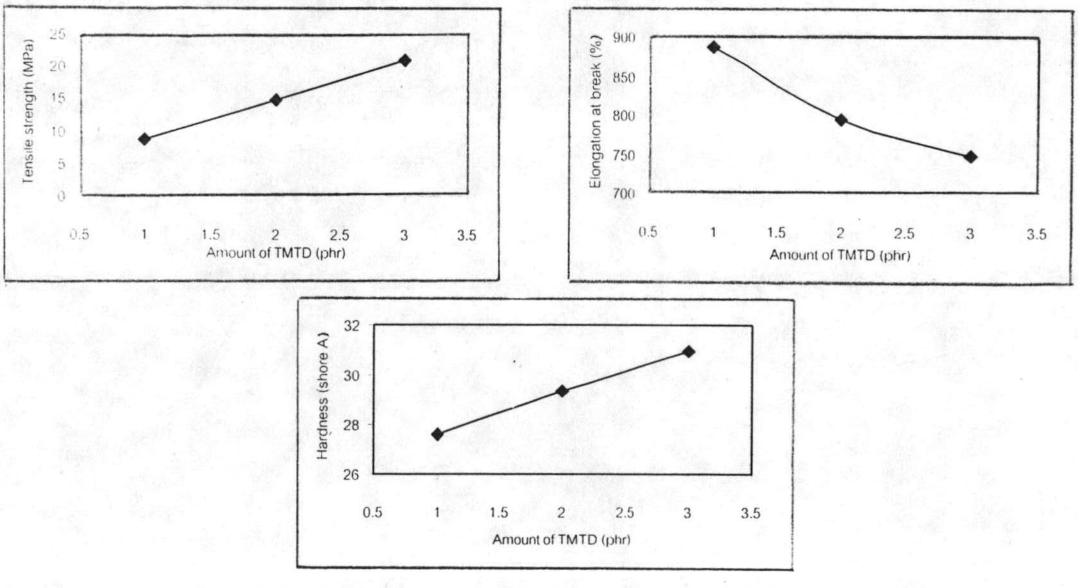

Figure 4.1 Effect of the amount of vulcanizing system at ammonium laurate 0.15 phr on the mechanical properties of vulcanized rubber

Table 4.9 Effect of the amount of vulcanizing system at tergitol NP9 0.5 phr on the mechanical properties

Properties	Test methods	Amount of TMTD (phr)		
		1	2	3
Tensile strength (MPa)	ISO 37	14.57	15.36	20.42
Elongation at break (%)	ISO 37	938	850	773
Hardness (shore A)	ASTM D 2240	28.9	30.6	33.1

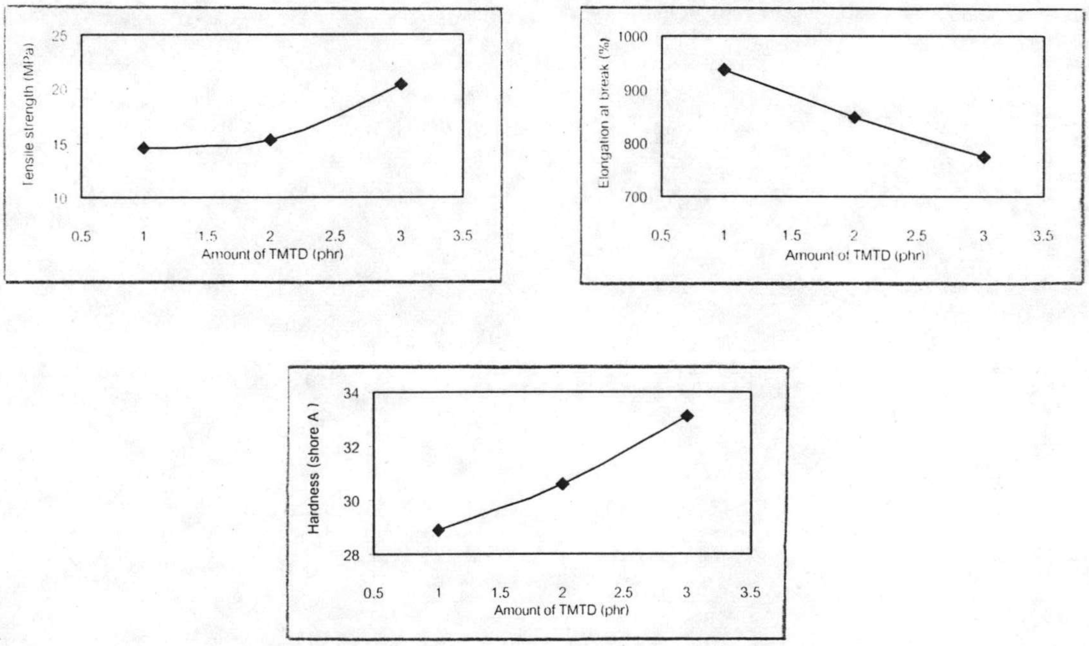

Figure 4.2 Effect of the amount of vulcanizing system at tergitol NP9 0.5 phr on the mechanical properties of vulcanized rubber

Table 4.10 Effect of the amount of vulcanizing system and type of surfactant on the adhesion strength of solder mask

Amount of TMTD (phr)	Adhesion strength (N)	
	Ammonium laurate	Tergitol NP9
1	110.3	45.03
2	97.85	30.44
3	68.8	27.48

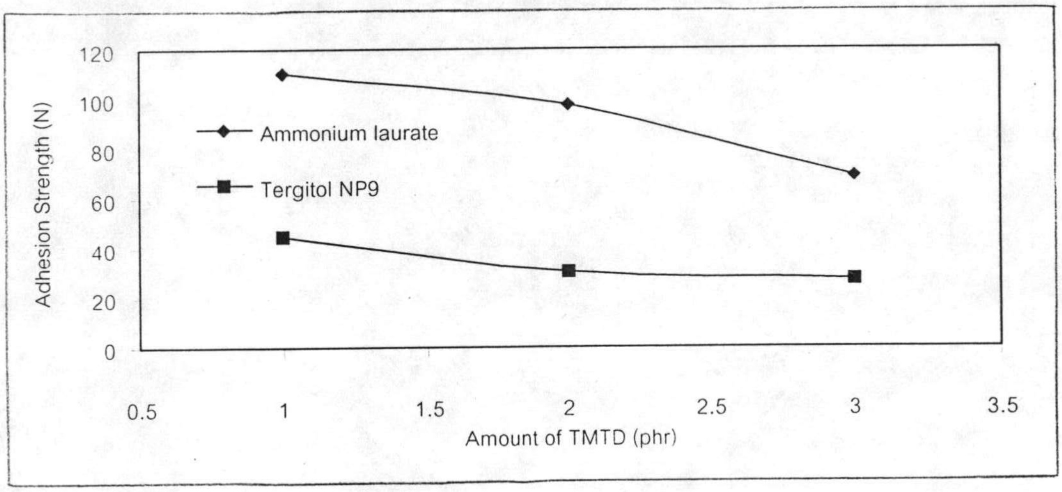

Figure 4.3 Effect of the amount of vulcanizing system and type of surfactant on the adhesion strength of solder mask

4.4 Effect of Amount of Titanium dioxide

The most effective white pigment available for latex work is rutile titanium dioxide. The effects of the amount of titanium dioxide on the properties of vulcanized rubbers were studied by varying the amounts of titanium dioxide to 1.25. 2.5 and 3.75 phr. The other ingredients were kept constant. The formulations of prevulcanized latex were obtained as follows:

60% Natural rubber latex		100	phr
15% Casein		0.75	phr
10% KOH		1	phr
Surfactant	- 25% Tergitol NP9,	0.5	phr
	- 20% Ammonium laurate	0.15	phr
Vulcanizing system			
50% ZnO		0.66	phr
50% TMTD		2	phr
33% ZBDC		0.66	phr
10% Thiourea		0.66	phr
Filler: 50% Titanium dioxide		1.25, 2.5, 3.75	phr

The mechanical properties of vulcanized rubbers and the physical property of the solder mask. which used ammonium laurate and tergitol NP9 as surfactants, were studied and the results are shown in Tables 4.11, 4.12.

Table 4.11 Effect of the amount of titanium dioxide at ammonium laurate 0.15 phr on the mechanical properties

Properties	Test methods	Amount of titanium dioxide (phr)		
		1.25	2.5	3.75
Tensile strength (MPa)	ISO 37	13.3	14.87	14.39
Elongation at break (%)	ISO 37	820	796	820
Hardness (shore A)	ASTM D 2240	27.8	29.4	31.1

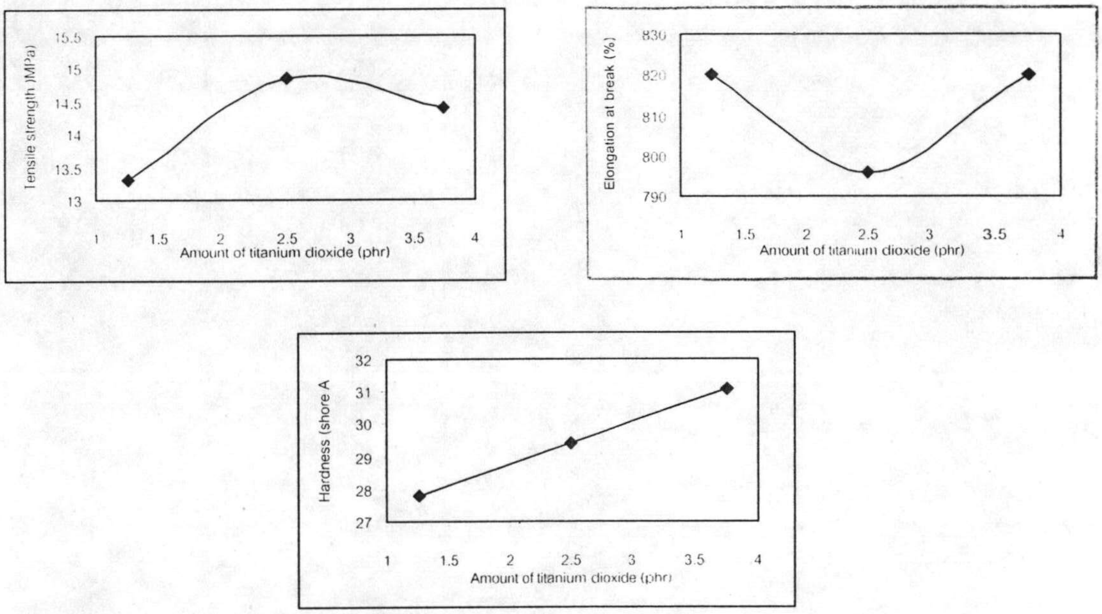

Figure 4.4 Effect of the amount of titanium dioxide at ammonium laurate 0.15 phr on the mechanical properties

Table 4.12 Effect of the amount of titanium dioxide at tergitol NP9 0.5 phr on the mechanical properties

Properties	Test methods	Amount of titanium dioxide (phr)		
		1.25	2.5	3.75
Tensile strength (MPa)	ISO 37	13.47	15.36	14.52
Elongation at break (%)	ISO 37	851	850	867
Hardness (shore A)	ASTM D 2240	26.9	30.6	34.5

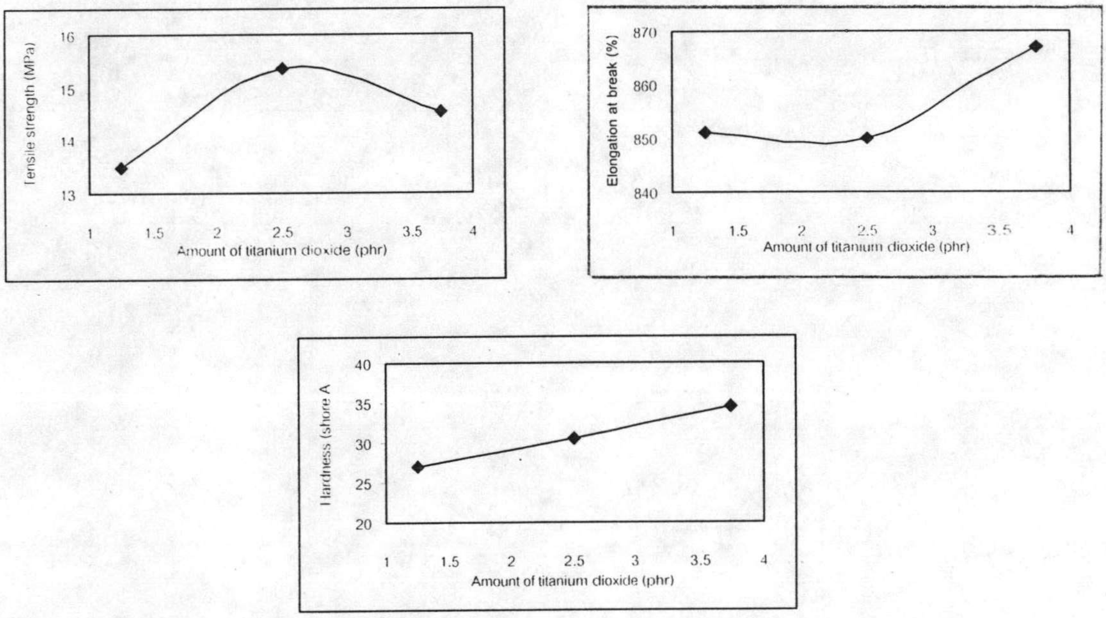

Figure 4.5 Effect of the amount of titanium dioxide at tergitol NP9 0.5 phr on the mechanical properties

From Tables 4.11, 4.12 and Figures 4.4, 4.5, the mechanical properties of the vulcanized sheets (tensile strength, elongation) were changed,a little when varying the amount of titanium dioxide. Increasing the amount of titanium dioxide lead to the increase of hardness of the vulcanized sheets. Titanium dioxide was the pigment added to the latex in order to color it. An ancillary effect, which may be exploited, is the effect, which stiffens the product, but has no effect analogous to the reinforcement of rubbers. Thus titanium dioxide does not enhance the tensile strength of vulcanized latex.

Table 4.13 and Figure 4.6 illustrate the effect of amount of titanium dioxide and type of surfactant on the adhesion strength of solder mask. The adhesion strength decreased with the increasing amount of titanium dioxide. It can be explained that the particles of rubber, which adhere with the surface of PCB, were replaced by the particles of titanium dioxide therefore the adhesion strength decreased.

Table 4.13 Effect of the amount of titanium dioxide and type of surfactant on the adhesion strength of solder masks

Amount of titanium dioxide (phr)	Adhesion strength (N)	
	Ammonium laurate	Tergitol NP9
1.25	142.5	37.01
2.5	97.85	30.44
3.75	94.03	21.53

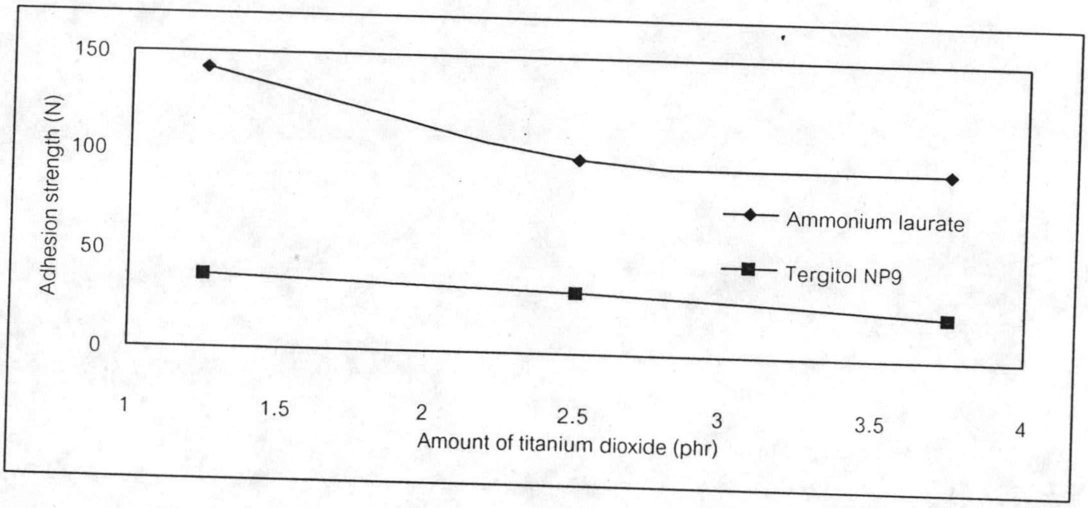

Figure 4.6 Effect of the amount of titanium dioxide and type of surfactant on the adhesion strength of solder mask

4.5 Effect of Thickener

In this experiment, carboxymethyl cellulose (CMC) was used as a thickener. CMC is soluble in water giving viscous solutions and is the principal application in latex technology, used as modifiers of bulk flow behavior. CMC was mixed with the prevulcanized latex, which was prepared from an appropriate formulation are shown below, by using a mechanical stirrer in order to make a homogeneous solder mask from natural rubber latex.

60% Natural rubber latex	100 parts by dry weight
15% Casein	0.75
25% Tergitol NP 9	0.5
10% KOH	1
50% ZnO	0.66

50% TMTD	2
33% ZBDC	0.66
10% Thiourea	0.66
50% Titanium dioxide	2.5

The effect of amount of CMC on the viscosity of solder masks is shown in Table 4.14. Brookfield viscometer model RVT small sample (spindle NO.14) was used to determine the viscosity of solder mask.

Table 4.14 Effect of the amount of CMC on the viscosity of solder masks

Amount of CMC (g per 100g of prevulcanized latex)	Viscosity (cps.)
5% CMC 20g	11,666.7
5% CMC 25g	12,843.8
6% CMC 20g	15,729.2
6% CMC 25g	19,281.3
7% CMC 20g	21,197.9
7%CMC 25g	26,562.5

From Table 4.14, the viscosity of solder masks increased with the increasing amount of CMC. When 5%CMC and 6%CMC were used to adjust the viscosity of solder mask, the viscosity was too low; thus, the control of flow became difficult. The appropriate amount of the thickener used was 7% 20-25g, preferably 25g per

100g of the prevulcanized latex. Alternations of viscosity of solder masks determined the viscosity in 2 months.

Table 4.15 Alternation of viscosity of solder masks in 8 weeks

Amount of CMC (g per 100g of prevulcanized latex)	Time (week)					
	0	1	2	4	6	8
5% CMC 20g	11,750.0	10,312.5	10,166.7	9,520.8	9,208.3	9,145.8
5% CMC 25g	12,979.2	12,000.0	12,458.3	11,291.7	11,250.0	11,312.5
6% CMC 20g	15,791.7	15,958.3	15,520.8	14,604.2	14,875.0	14,729.2
6% CMC 25g	19,333.3	19,250.0	19,333.3	17,395.8	16,937.5	17,020.8
7% CMC 20g	21,187.5	21,958.3	21,520.8	19,854.2	20,791.7	20,833.3
7% CMC 25g	26,645.8	25,395.8	26,583.3	25,208.3	25,645.8	25,729.2

As shown in Table 4.15, the viscosity of solder masks tended to be constant through 8 weeks. It can be explained that the stability and pH of ingredient dispersion were comparable with rubber latex. The ingredients did not disturb the acid-base equilibrium. Therefore, solder masks in this study had good stability and can be used in the electronic industry.

4.6 Thermal Properties of Solder Mask

In this study, a Thermogravimetric Analyzer (TGA) was used to obtain the initial degradation temperature (T_{onset}) and the temperature of the maximum degradation rates (T_{max}). TG/DTG thermogram of solder mask that was prepared from a suitable formula of prevulcanized latex is shown in Appendix E. TG/DTG curves showed a continual weight loss over the temperature range 100-600°C. The TGA measurements showed that T_{onset} and T_{max} of solder mask were 381.82 and 401.13°C, respectively; when compared with T_{max} of natural rubber was 373°C [18].

In the electronic industry[19], solders do not have a melting point with the exception of eutectic compositions. They have a solidus temperature below which the solder is solid and a liquidus temperature above which the solder is liquid. Between these two temperatures-the difference is dependent upon how close the composition is to eutectic-the solder is pasty and does not flow. For example, the solidus temperature for Sn/Pb solders is 183 °C, but the liquidus temperature can vary from 183°C to 232°C for Sn-rich compositions and 328°C for Pb-rich solders. The most important quality of a solder joint is good wetting to the base metals of the PCB and component. These base metals are, in most cases, Cu and Alloy 42 (42% nickel and iron). Cu and Alloy 42 require a higher temperature at reflow for good wetting. Typically, this is about 20°C above liquidus for Cu and 35°C for Ni and Ni alloys.

The comparison of T_{onset} of solder mask and the minimun reflow temperatures of some common solders were 381.82 and 203-224°C, as such the solder mask could resist to soldering.

Table 4.16 Liquidus and minimum reflow temperatures for some common solders [20].

Solder	Liquidus temperature	Minimum reflow temperature	
		Copper	Alloy 42
63Sn/37Pb	183°C	203°C	218°C
60Sn/40Pb	188°C	208°C	223°C
62Sn/36Pb/2Ag	189°C	209°C	224°C