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Heat Sensitized Dipping with Radiation Vulcanized Natural Rubber Latex

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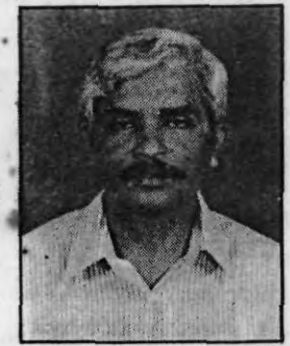

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Abstract

Dipping is an important process in latex technology for the production of articles like examination gloves, teats, condoms, catheters etc. Straight dipping is used for the production of very thin walled articles. Coagulant dipping provides little more thicker articles; but a number of dips are needed to achieve desired thickness.

The use of radiation vulcanized natural rubber latex (RVNRL) is becoming more popular in areas where dipped products free from type IV allergy, carcinogenic nitrosamines and very low in type I allergy are required. The common dipping processes with RVNRL are straight and coagulant dipping. This paper describes the results of heat sensitive dipping experiments for obtaining dry deposits of thickness 2-4 mm in single dip. The effects of dwell time, temperature of the former and maturity of latex compound at the time of dipping have been studied. The storage stability of the dry latex compound and the tensile properties of the dry deposits are good.

Key words : RVNRL – Heat sensitive dipping

Introduction

Dipped products form the largest sector of the latex industry, dealing with the production of articles like different types of gloves, condoms, teats, soothers, catheters etc.[1] Makuuchi has highlighted the advantages of RVNRL[2]. The major ones are absence of type IV allergy due to compounding chemicals[3], very low cytotoxicity[4,5], absence of carcinogenic nitrosamines[6] and low in extractable protein (EP) content[7,8]. Several papers have been published on the coagulant dipping process with RVNRL[6,9,10]. Heat sensitized dipping is a process in which thick deposits are produced in a single dip and several authors have described this process in the case of sulphur vulcanized natural latex[9,11-17]. The ideal heat sensitizing agent should meet the following three requirements[13]

(i) It should be possible to store the latex compound at room temperature without any change in its properties.

(ii) It should be possible, by raising the temperature, to obtain in a short time a gel of uniform structure.

(iii) The agent should not change the viscosity or mechanical stability of the latex.

However published information on heat sensitive dipping with RVNRL is very limited[6]. RVNRL processed with n-butyl acrylate (nBA) as sensitizer contains appreciable quantities of potassium hydroxide, a strong alkali, as stabilizer[18]. The pH of potassium hydroxide stabilized RVNRL is high and hence the conventional heat sensitizing methods applied for sulphur vulcanized latex are unsuccessful. Thomas[19] has recently reported the comparative economics of sulphur prevulcanized latex and RVNRL. It is observed that RVNRL is more costly. If one can reduce the number of dips to achieve a given thickness, the labour component of the dipping process can be reduced. Thus heat sensitive dipping can reduce the cost of the dipping process. Hence studies were undertaken to develop suitable systems for heat sensitive dipping of RVNRL.

EXPERIMENTAL

RVNRL used in this study was processed by methods previously reported[20]. A combination of zinc ammine and polyvinylmethyl ether (PVME) systems was used in this study. Dipping was carried out for several combinations of zinc ammine and PVME concentrations. One among the promising combinations, whose formulation is given in table 1 was used for detailed evaluation. Other variables studied were the effects of dwell time, age of latex compound at the time of dipping and temperature of the former. Withdrawal of the former was carried out at high speed so as not to permit any latex to adhere to the gelled mass on the former. The deposits were subjected to wet gel leaching for 10 min in water at 30°C and then dried at 70°C. Due to the inverse solubility of PVME, leaching was carried out at room temperature only. The thickness of the dry films were determined. The stability of the latex compound was ascertained by measuring its viscosity with a Brookfield viscometer, using spindle number 2. Tensile properties of the dry deposits were determined using standard procedures.

Table 1
Latex compound for heat sensitized dipping

Ingredient	*Dry weight*	*Wet weight*
50% RVNRL	100	200
10% Ammonium acetate	0.5	5
50% Zinc oxide	0.5	1
10% PVME	1.0	10

RESULTS AND DISCUSSIONS

Zinc ammine-PVME Composite System

When Zinc oxide is added to ordinary ammoniated latex a gradual increase in viscosity is observed. The following equations represent the chemical reactions leading to the dissolution of zinc as zinc ammine in the aqueous phase of latex[21].

$$ZnO + H_2O \rightleftharpoons Zn(OH)_2 \qquad (1)$$

$$Zn(OH)_2 \rightleftharpoons Zn^{+2} + 2OH^- \qquad (2)$$

$$Zn^{+2} + n\,NH_3 \rightleftharpoons [Zn\,(NH_3)_n]^{+2} \qquad (3)$$

The zinc ammines are thermally unstable and decompose on heating to zinc ions which is turn form insoluble zinc soaps/proteinates by reaction with higher fatty acid/protein anions.

$$[Zn\,(NH_3)_n]^{+2} \rightleftharpoons Zn^{+2} + n\,NH_3 \qquad (4)$$

$$Zn^{+2} + 2RCOO^- \rightarrow (RCOO)_2\,Zn \qquad (5)$$

Initial attempts to prepare heat sensitive RVNRL using zinc ammine system were not very successful, probably because of the high concentration of hydroxyl ions (OH^-) originating from potassium hydroxide, added as stabilizer, since high concentration of OH^- ions retard the dissolution of zinc oxide. The solubility of zinc oxide in aqueous solutions of ammonia and ammonium salts, is predominantly as zinc tetrammine, $Zn(NH_3)_4^{+2}$ and its concentration is found to be proportional to the product of the squares of concentrations of ammonia and ammonium ions[22]. In RVNRL the availability of ammonium ions is suppressed by hydroxyl ions. To suppress the concentration of hydroxyl ions, ammonium ions are deliberately added, as ammonium acetate, so that the concentration of soluble zinc increases.

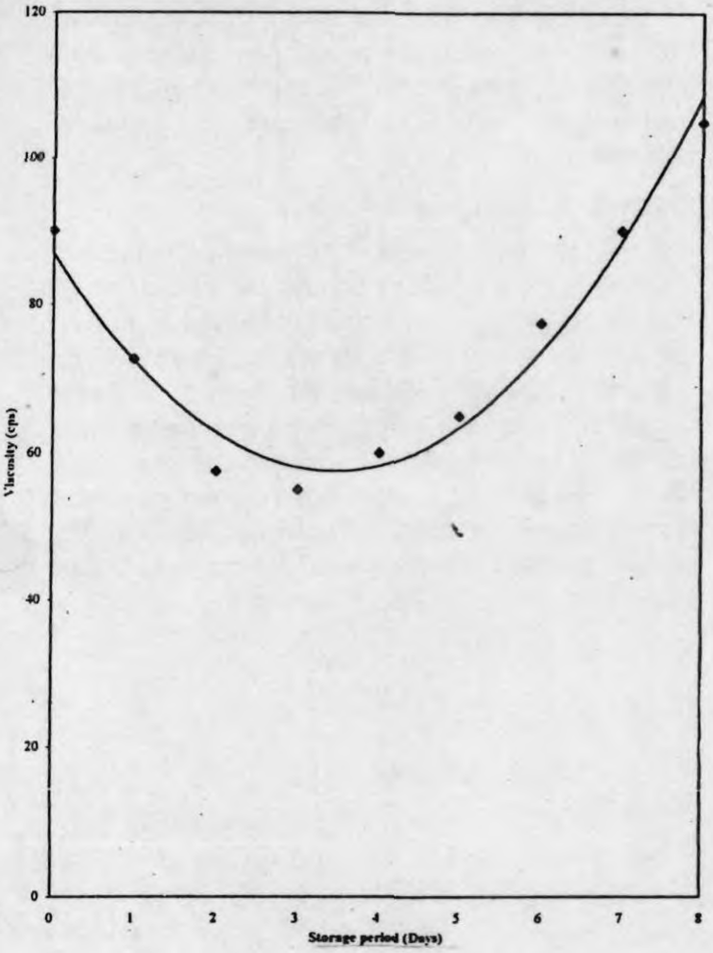

Fig. 1. Variation of viscoty of latex compound during storage.

Polyvinylmethyl ether (PVME) is a water-soluble polymer, having molecular structure similar to that of non-ionic surfactants and hence PVME also is surface active to some extent; however the absence of any large hydrophobic groups indicate that this activity is not too high. The solubility of PVME in water is due to hydrogen bonding between water molecules and oxygen atoms of the ether group. Hydrogen bonds are very sensitive to temperature and PVME precipitates from aqueous solutions at about 34°C[23].

In RVNRL, use of PVME alone as heat sensitising agent also was not successful. However a combination of zinc ammine and PVME systems was found to be suitable for heat sensitive dipping of RVNRL.

Stability of Heat Sensitive Latex Compound

Viscosity of the latex compound was assessed to evaluate the storage stability of compounded latex. Changes in the viscosity of the latex compound in a period of 8 days is given in figure 1. It can be seen that viscosity decreases initially for a few days and then progressively increases. The fall in viscosity is probably due to some agglomeration of the particles through absorbed PVME molecules. One short-coming of zinc ammine system is that they destabilise latex slowly even at room temperature[14]. This probably contributes to the increase in viscosity during storage.

Effect of Dwell Time in Heat Sensitive Dipping

Fig. 2 gives the effect of dwell time (D) on thickness of dry film (t) when dipping was carried out at 70°C, using heat sensitive latex compound of different maturities. It is observed that thickness of the dry latex film increases with dwell time. However the rate of increase of dry film thickness decreases with increase in dwell time. Fig. 3 shows the variation of thickness of

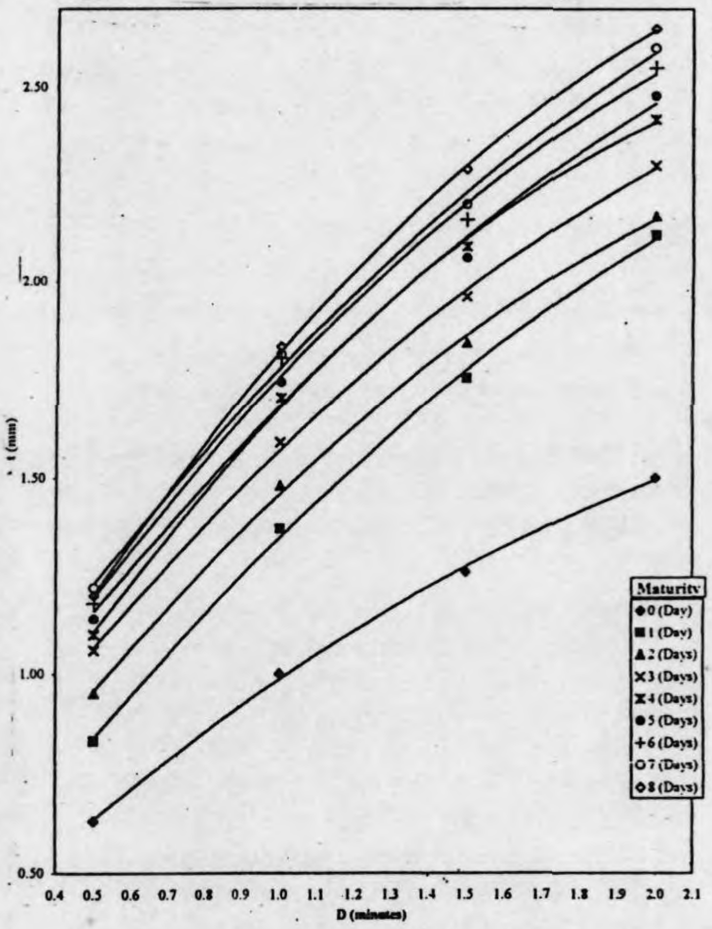

Fig. 2. Variation of thickness of RVNRL film (t) Vs dwell time (D) (dipping at 70°C)

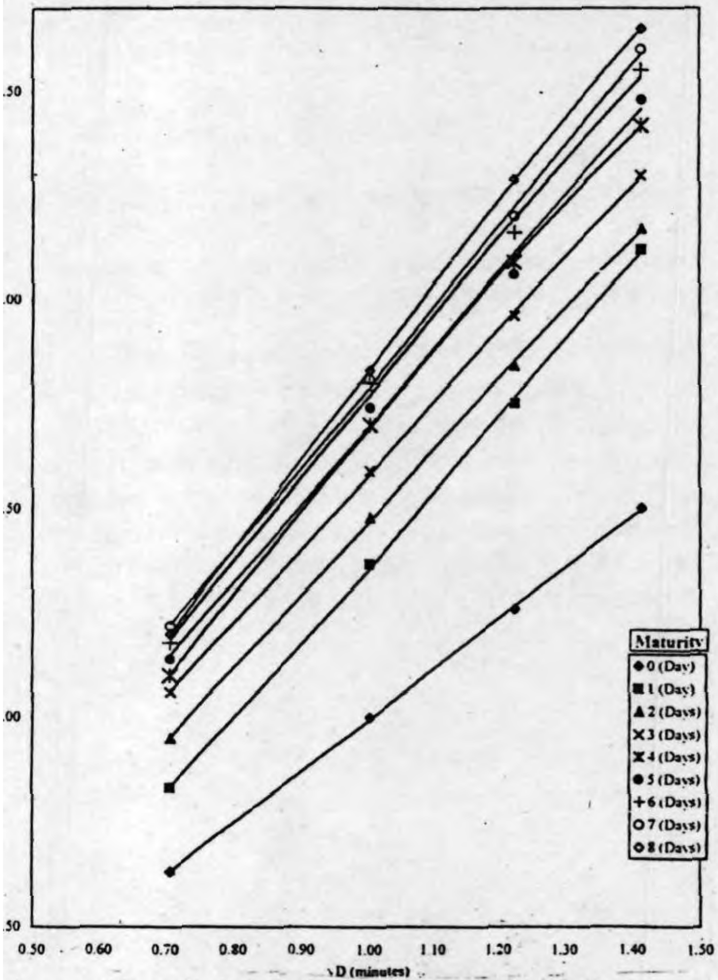

Fig. 3. Variation of thickness of RVNRL film (t) Vs square root of dwell time (√D) (dipping at 70°C)

dry deposit against square root of dwell time. More or less a linear relation is observed. A similar behaviour has been reported in coagulant dipping of natural latex[24].

The fall in the rate of increase in thickness with dwell time is probably due to dissipation of heat in to a larger area when heat travels radially outward from a cylindrical former and also due to the fall in the effective temperature of the former when the near by latex is getting heated up. In the present study, one cannot identify separately the contribution of the zinc ammine and PVME to the formation of gelled latex films. Reaction of the zinc ammines with the adsorbed anions at the rubber-water interface, results in the neutralisation/reduction of the surface charge on the particles resulting in lesser repulsive force between them leading to destabilisation of latex in the region. At temperatures above about 34°C, PVME precipitates from solution[14] and forms a separate phase of high surface area. This extra surface competes with rubber particles for colloidal stabilisers and leads to destabilisation.

Effect of Temperature of Former

It has been reported that PVME precipitates almost completely from aqueous solution at about 34°C[14]. However dipping as per formulation given in Table 1 were not found to be practically useful below 50°C. Fig. 4 shows the variation of thickness of dry deposit with temperature for various dwell times using latex compound immediately after preparation and Fig. 5 shows the behaviour of same latex compound after 4 days of storage. It is observed that thickness of the dry deposit increases with temperature. The rate of increase in thickness of deposit with dwell time also increase as

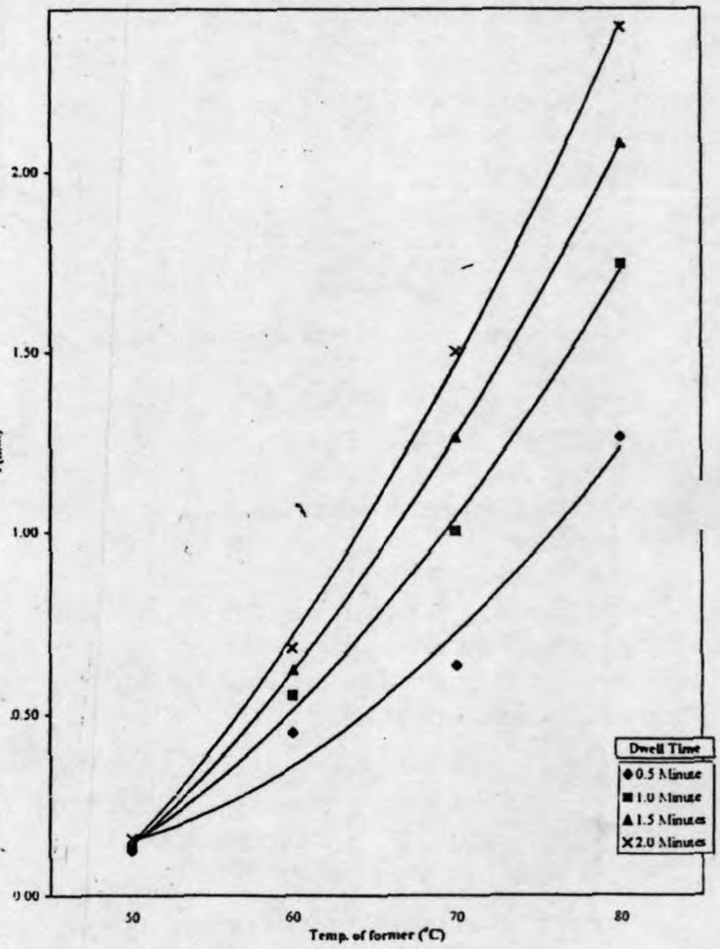

Fig. 4. Effect of temperature of former on thickness (t) of the dry deposit (dipping immediately after compounding)

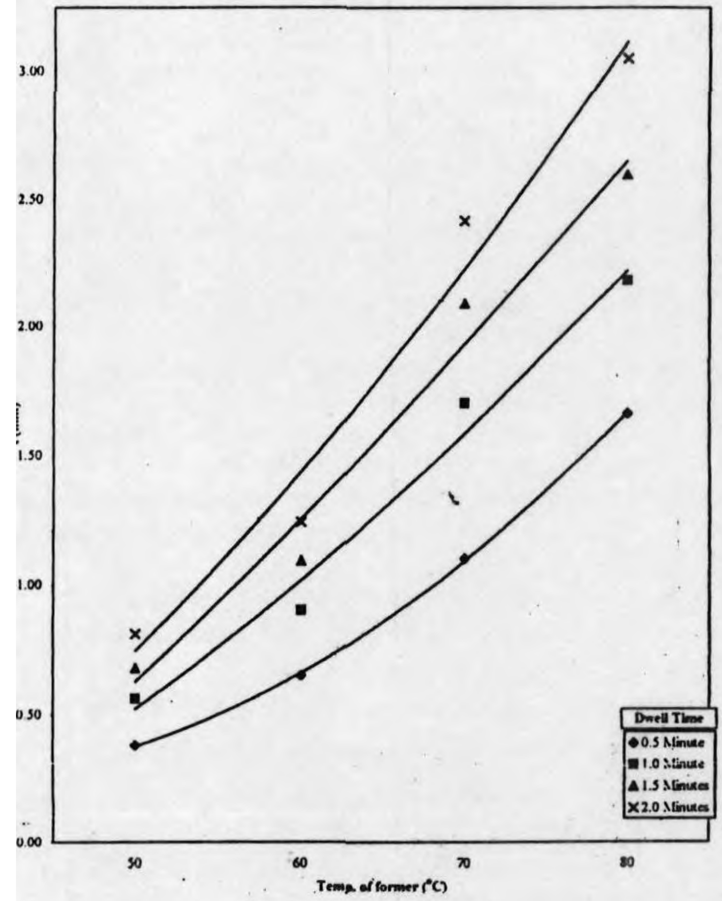

Fig. 5. Effect of temperature of former on thickness (t) of dry deposit (maturity of latex compound 4 days)

the temperature of the former is increased. The lower thickness at all temperatures of dipping using latex compound immediately after compounding, compared to matured compound indicates that the mechanism of destabilisation initially operating is probably only via the zinc ammine, due to the time involvement for adsorption of PVME at rubber-serum interface. Maximum temperature of dipping was limited to 80°C, since the latex show signs of complete destabilization above this temperature. The increased deposit thickness at higher temperature is attributed to the less stability of zinc ammines at elevated temperatures and also due to the increased tendency of PVME to precipitate at elevated temperatures.

Effect of Maturity of Latex Compound

Fig. 2 also shows the behaviour of latex compound immediately after compounding up to a storage of 8 days and Fig. 6 shows the variation of thickness of deposit with maturity of latex compound for different dwell times when dipped at 70°C. It is observed from Fig. 2 that the latex compound immediately after compounding behaves rather differently compared to matured latex of storage period 1-8 days. This may probably be due to time interval needed for PVME to get adsorbed at the rubber - serium interface from the aqueous phase. From Fig. 6 it is seen that thickness of deposit increases progressively with maturity. Increase in viscosity of latex compound during storage is one of the factors contributing to increased thickness of dry deposit. Increase in thickness due to storage of latex compound almost ceases after 8 days. This may probably be due to the poor thermal conductivity of the gelled material. After 12 days of storage at 28°C, latex compound exhibits signs of destabilisation and after 18 days latex compound was fully coagulated.

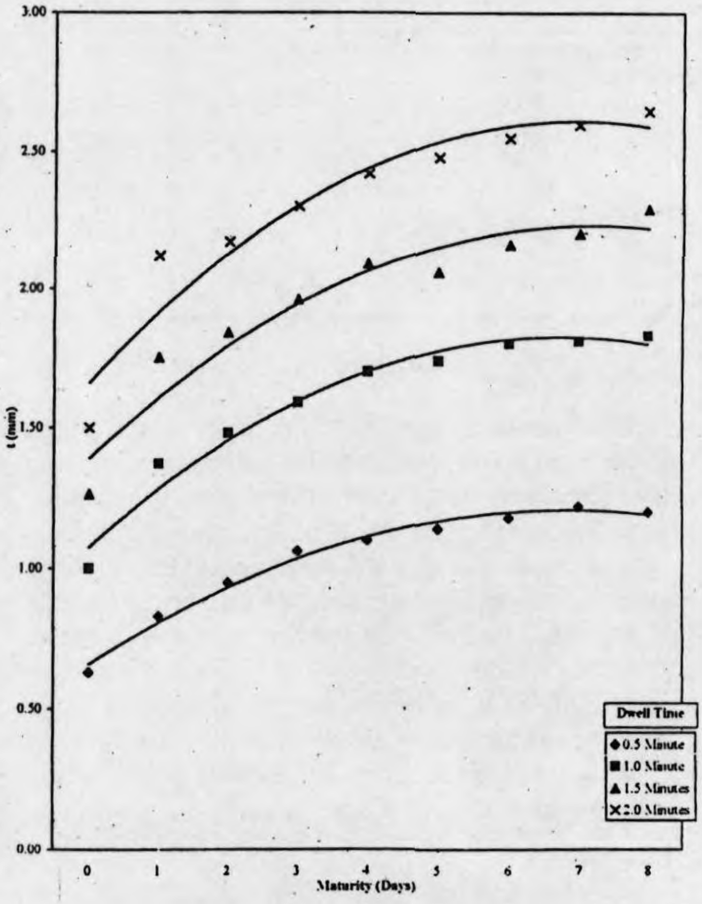

Fig. 6. Effect of maturity of latex compound on thickness (t) of dry deposit (dipping at 70°C)

Tensile Properties of Dipped Films

Table 2 shows the tensile properties of latex films prepared by heat sensitive dipping, both before and after leaching. Considering the high thickness of the deposit wet gel leaching was adopted. Tensile properties are generally low before leaching. During leaching the non rubber materials adsorbed at the rubber-serum interface are removed, so that better integration of the particles are possible[25], resulting in improved tensile properties. Even though the tensile strength of the leached films are less than that of coagulant dipped films, tensile strength of the order of 24-25 MPa is sufficient for common thick articles that can be produced by heat sensitive dipping.

Table 2

Physical properties of RVNRL films produced be heat sensitive dipping

Property	*Before leaching*	*After leaching*
Modulus (MPa)		
M_{100}	0.605	0.732
M_{300}	0.995	1.259
M_{500}	1.519	2.167
Tensile strength (MPa)	18.58	24.33
Elongation at break (%)	1168	1080

Conclusions

A composite system, containing zinc ammine and PVME has been standardised for heat sensitive dipping to produce thick films out of radiation vulcanized natural latex. Thickness of the dry deposit increases with dwell time, temperature of the former and maturity of the latex compound. Similar to coagulant dipping, thickness of dry film bears a linear relation with square not of dwell time. Thickness of deposit increases with increase in maturity of latex compound up to about 4 days. Further maturation has practically no effect on thickness. The latex compound exhibits good storage stability and leached films show good tensile properties.

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