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# Effect of Prevulcanisation of Natural Rubber Latex on the Chemical and Physical Properties of Latex Thread

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## Synopsis

The effect of prevulcanisation on the processing properties and network structure of a series of latex compounds containing conventional and efficient vulcanisation (E.V. systems) systems for the manufacture of latex thread was evaluated. Prevlcanisation was effected at 70°C and the extent of crosslinks formed and compound viscosity at various periods of heating were studied. It is observed that the vulcanisation systems studied have a profound effect on the extent of crosslink formation during prevulcanisation. The network structure of the vulcanisate was also studied and found that polysulphidic content is high as the extent of prevulcanisation of the latex compound increases. Latex threads were also prepared from typical latex compounds which were prevulcanised to different degrees and their chemical and physical properties were evaluated. It is observed that the extent of prevulcanisation affects the aged and unaged physical properties of latex threads.

## INTRODUCTION

For obtaining good processing and technological properties for latex thread a certain extent of prevulcanisation is essential for the rubber particles in the latex compound.<sup>1</sup> Prevlcanisation involves heating the raw latex with various compounding ingredients such as accelerator and sulfur at or around 70°C until the required degree of crosslinking is obtained.<sup>2,3</sup> The rate of prevulcanisation varies with different vulcanisation systems and the extent of prevulcanisation has a profound effect on the final vulcanisate properties.<sup>3</sup> It has been reported that prevulcanised latex films are inferior in properties and are less resistant to heat and solvent.<sup>3</sup> Studies conducted in this line are based on general vulcanisation systems only.<sup>4,5</sup>

To meet quality requirements for the thread, different accelerators or their combinations are used in the vulcanisation system.<sup>6,7</sup> The important quality requirements for latex thread include diameter (count), tensile strength, modulus, elongation at break, and aging resistance.<sup>8</sup>

This paper reports the results of our studies on prevulcanisation of a series of latex compounds containing conventional and efficient vulcanisation systems (E.V. system) for the manufacture of latex thread. In the first part, the effect of different vulcanisation systems on the extent of crosslinks formed and viscosity of latex compounds at various periods of prevulcanisation and the network structure of the vulcanisates were studied. In the second part, typical latex compounds were prevulcanised to different durations and used in the prepa-

TABLE I  
Formulations of Latex Compounds (Conventional Vulcanisation Systems)

Compounds	A	B	C
60% Centrifuged latex	167	167	167
10% Potassium hydroxide solution	1	1	1
10% Potassium laurate solution	2	2	2
50% Sulfur dispersion	3.5	3.5	3.5
50% Zinc diethyl dithio carbamate (ZDC) dispersion	4.0	3.0	3.0
50% Zinc mercapto benzothiazole (ZMBT) dispersion	—	1.0	—
50% Tetra methyl thiuram disulphide (TMTD) dispersion	—	—	1.0
50% Anatase titanium dioxide dispersion	10	10	10
50% Antioxidant SP emulsion	2	2	2
50% Zinc oxide dispersion	0.8	0.8	0.8

ration of latex threads and the effect of prevulcanisation on the aged and unaged physical properties of latex threads were studied.

## EXPERIMENTAL

The formulations of latex compounds used in this study are given in Tables I and II. Centrifuged natural rubber latex (HA type) with 60% dry rubber content conforming to BIS : 5430-1981 was used for preparing the compounds. Vulcanising agents and pigments were added as fine dispersions prepared by ball milling. Antioxidant SP was added as an emulsion. The latex compounds were prepared as per the formulations and prevulcanised by heating under mild stirring in a glass beaker immersed in a constant temperature bath set at 70°C. Samples of latex compounds were taken at definite intervals for studying its processing behaviour, extent of crosslink formation, and to prepare threads for technical evaluation.

TABLE II  
Formulations of Latex Compounds (Efficient Vulcanisation Systems)

Compounds	D	E	F
60% Centrifuged latex	167	167	167
10% Potassium hydroxide solution	1	1	1
10% Potassium laurate solution	2	2	2
50% Sulfur dispersion	0.5	0.5	0.5
50% Tetra methyl thiuram disulphide (TMTD) dispersion	6.0	6.0	6.0
20% Thiourea solution	5.0	5.0	5.0
50% Zinc diethyl dithio carbamate (ZDC) dispersion	4.0	—	3.0
50% Zinc mercapto benzothiazole (ZMBT) dispersion	—	4.0	1.0
50% Antioxidant SP emulsion	2.0	2.0	2.0
50% Anatase titanium dioxide dispersion	10	10	10
50% Zinc oxide dispersion	0.8	0.8	0.8

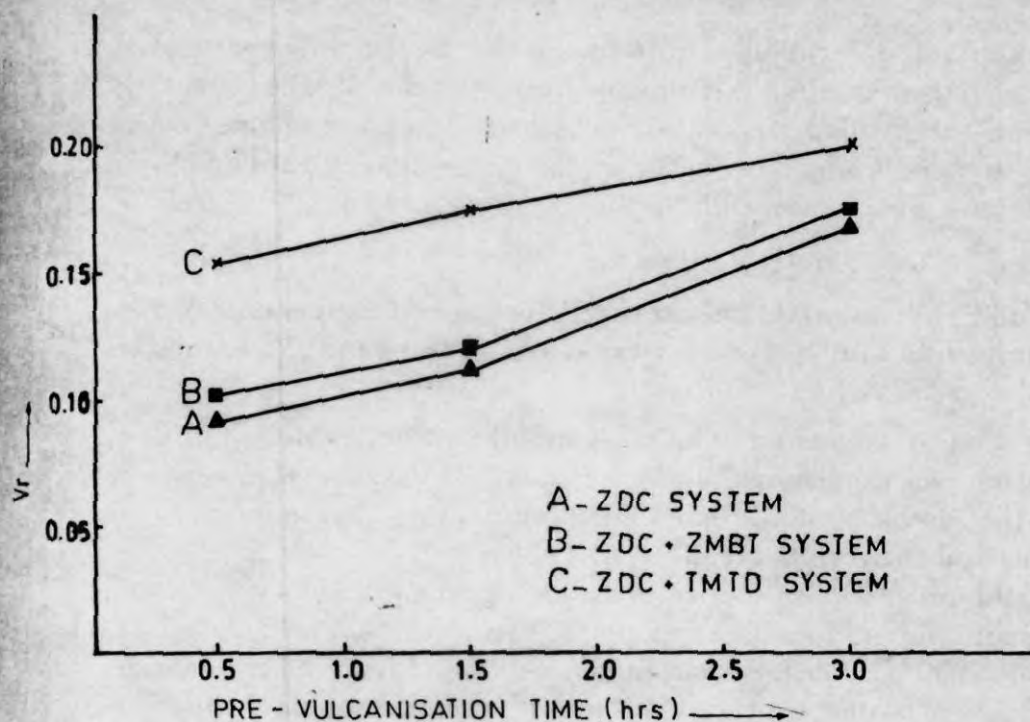


Fig. 1(a). Plot of chemical crosslinks ( $V_r$ ) versus prevulcanisation time in the conventional systems.

#### Effect of Vulcanisation System on the Extent of Crosslink Formation

The crosslink formation at each interval of heating was measured after preparing latex films at room temperature on glass cells. Each sample weighing 0.2 to 0.3 g was allowed to swell in an excess of benzene containing 0.5% N-

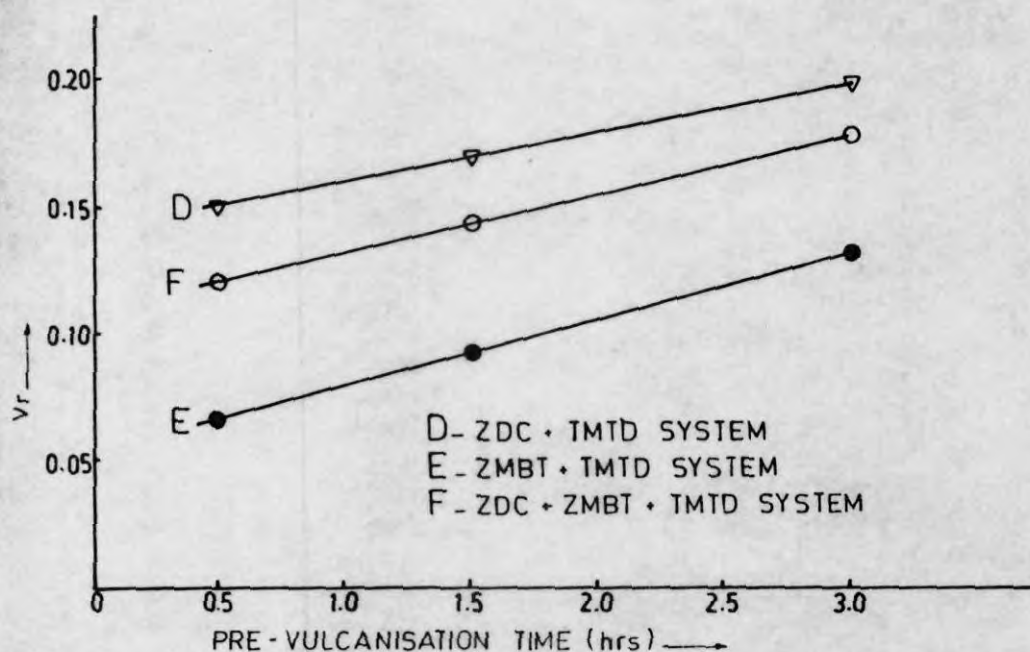


Fig. 1(b). Plot of chemical crosslinks ( $V_r$ ) versus prevulcanisation time in efficient systems.



phenyl- $\beta$ -naphthylamine at 30°C for 48 h. The swollen sample was weighed, the solvent removed *in vacuo*, and the sample weighed again.  $V_r$ , the volume fraction of rubber in the swollen vulcanisate, which is a measure of total number of crosslinks, was determined using the method suggested by Ellis and Welding.<sup>3</sup> The results are given graphically in Figures 1(a) and (b).

### Effect of Prevulcanisation on the Rheological Behaviour of Latex Compounds and Network Structure of the Final Vulcanisate

The rheological behaviour of latex compounds after definite intervals of prevulcanisation was determined using a Brookfield viscometer (spindle no. 2). For this the viscosity of the latex compounds were determined at different shear rates and the results are given in Table III.

The optimum vulcanisation times for the dried latex films were determined by vulcanising them in an air oven at 100°C for different periods and then by plotting ' $V_r$ ' against vulcanisation time as given in Figure 2. Also included is a plot of  $V_r$  against vulcanisation time for the case of compound which was not prevulcanised. Network structure of the dried films obtained at different periods

TABLE III  
Rheological Behaviour of Latex Compounds

Compound	Duration of heating at 70°C (hrs)	Brookfield viscosity (CPS)	
		6 r.p.m.	60 r.p.m.
A	1	100	55
	$\frac{1}{2}$	125	60
	$1\frac{1}{2}$	130	65
	3	150	72
B	0	100	55
	$\frac{1}{2}$	128	61
	$1\frac{1}{2}$	135	67
	3	155	74
C	0	100	55
	$\frac{1}{2}$	120	60
	$1\frac{1}{2}$	145	68
	3	200	75
D	0	100	55
	$\frac{1}{2}$	120	60
	$1\frac{1}{2}$	135	65
	3	175	75
E	0	100	55
	$\frac{1}{2}$	130	65
	$1\frac{1}{2}$	140	68
	3	160	78
F	0	100	55
	$\frac{1}{2}$	120	60
	$1\frac{1}{2}$	140	68
	3	175	75

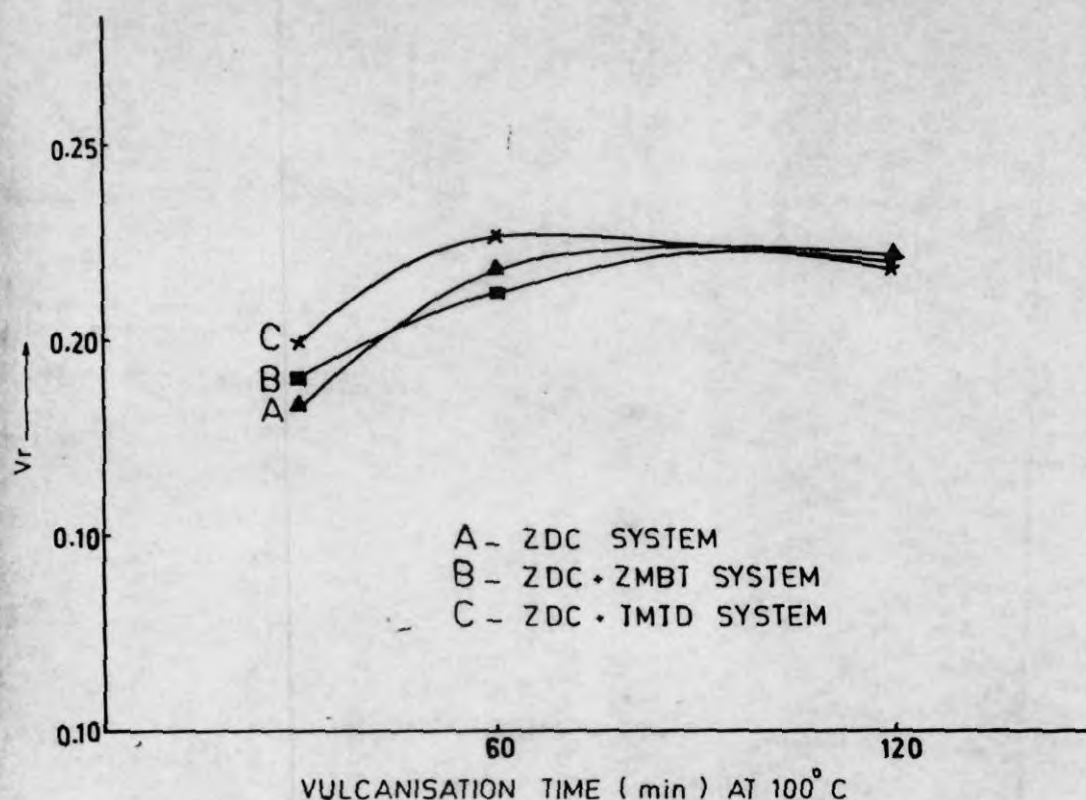


Fig. 2(a). Plot of chemical crosslinks ( $V_r$ ) versus vulcanisation time in the conventional systems.

of prevulcanisation were determined only after vulcanisation at  $100^\circ\text{C}$  in an air oven to the optimum level as determined earlier. For determining the polysulphidic content of the vulcanisates, each sample weighing 0.2 to 0.3 g was treated with a solution of propane-2-thiol (0.4M) and piperidine (0.4M) in *n*-heptane for 2 h at room temperature under nitrogen. The samples were washed with petroleum ether (bp  $40\text{--}60^\circ\text{C}$ ) and dried *in vacuo*. The polysulfidic crosslinks were obtained by the difference between the values of total crosslink concentration (measured as  $V_r$  values) before and after treatment.<sup>10</sup> The results are given in Table IV.

### Production and Testing of Latex Threads

To study the effect of prevulcanisation on technical properties, latex threads were prepared from prevulcanised latex compounds collected at different durations of heating. Compound B having a conventional vulcanisation system and compound F having an efficient vulcanisation system (E.V. system) were selected for the preparation of threads. Four threads were taken from each latex compound which was prevulcanised for four different times ( $0$ ,  $\frac{1}{2}$ ,  $1\frac{1}{2}$ , and 3 h). A schematic diagram of the process is given in Figure 3. The latex compounds were extruded through a glass capillary of 0.6 mm diameter into an acid bath containing 20% formic acid, washed in hot water at  $70^\circ\text{C}$ , dried in a hot chamber at  $90^\circ\text{C}$  and the threads were collected in aluminium trays, after dusting with talc, and then wound on wooden frames. Latex thread obtained

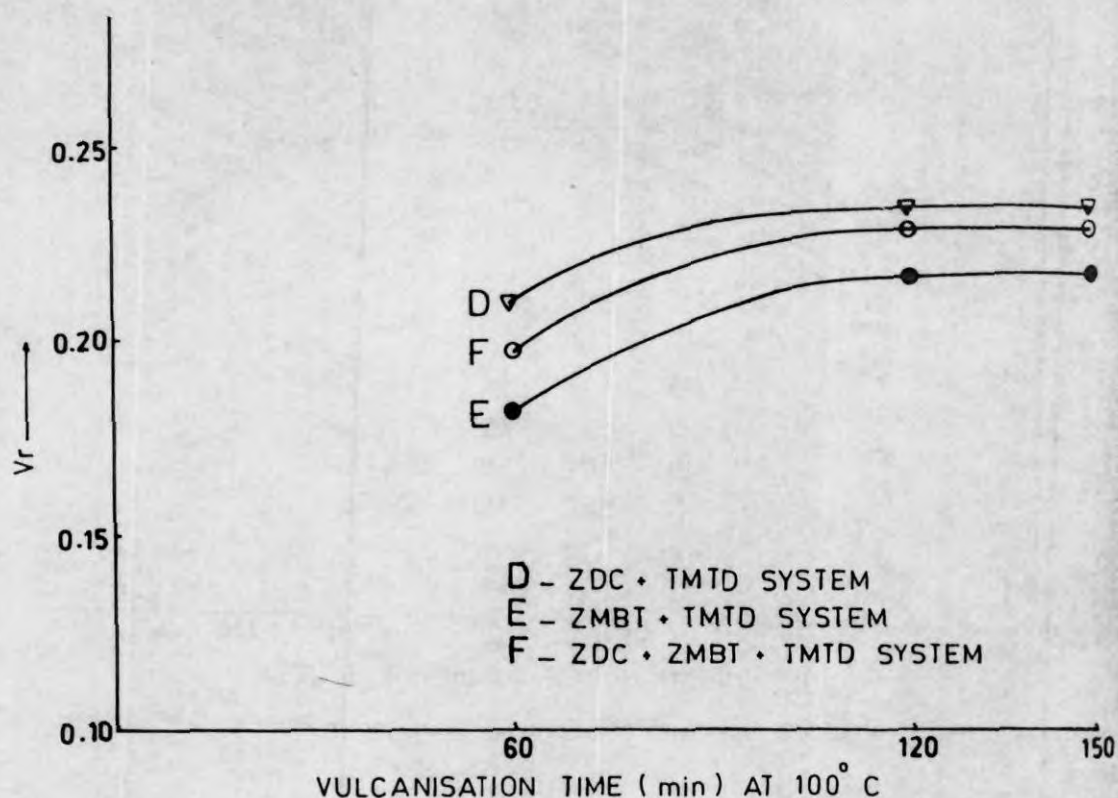


Fig. 2(b). Plot of chemical crosslinks ( $V_r$ ) versus vulcanisation time in the efficient systems.

from each compound was again vulcanised in an air oven at 100°C till optimum vulcanisate properties were obtained.

Testing of the thread was carried out according to ASTM D 2433-70. Five test pieces were taken from each sample and were tested for tensile properties, according to ASTM D 412, using a Zwick Universal Testing machine. In order to assess the aging resistance, the threads were aged at 100°C for 22 h in an air oven. In case of heat resistant threads produced using EV systems, aging was conducted at 150°C for 2 h in an air oven using ASTM D 3854-79. The aging resistance of the thread produced from each formulation was assessed according to the retention of its tensile properties after aging. The results are given in Tables V and VI.

## RESULTS AND DISCUSSION

The extent of crosslink formation at different periods of prevulcanisation at 70°C are given in Fig. 1(a) and (b). In the compounds containing conventional vulcanisation systems, A, B, and C, the reaction rate of the accelerator ZDC is increased by the incorporation of ZMBT (B) and TMTD (C). The ZDC-TMTD system (C) has a higher reaction rate than the ZDC-ZMBT system (B) and in the former system the majority of the crosslinks are formed within one and a half hour at 70°C. This may be attributed to the positive synergistic effect due to the combination of two ultra accelerators—ZDC and TMTD.

In the efficient vulcanisation systems, D, E, and F, the ZDC-TMTD system (D) is faster compared to ZMBT-TMTD system (E) in the formation of chem-



TABLE IV  
Effect of Prevulcanisation on Network Structure of the Vulcanisates

Compounds	Duration of heating at 70°C (hrs)	V <sub>r</sub> values		% polysulfidic crosslinks in the vulcanisates*
		Dried films	Vulcanisates*	
A	0	—	0.2203	20
	$\frac{1}{2}$	0.0881	0.2200	20
	$1\frac{1}{2}$	0.1116	0.2198	24
	3	0.1649	0.2210	32
B	0	—	0.2186	16
	$\frac{1}{2}$	0.1130	0.2180	16
	$1\frac{1}{2}$	0.1250	0.2184	18
	3	0.1662	0.2200	24
C	0	—	0.2260	18
	$\frac{1}{2}$	0.1597	0.2270	22
	$1\frac{1}{2}$	0.1800	0.2288	28
	3	0.1957	0.2272	34
D	0	—	0.2270	10
	$\frac{1}{2}$	0.1500	0.2260	12
	$1\frac{1}{2}$	0.1724	0.2250	12
	3	0.2004	0.2280	15
E	0	—	0.2140	8
	$\frac{1}{2}$	0.0760	0.2130	10
	$1\frac{1}{2}$	0.1093	0.2145	12
	3	0.1308	0.2099	14
F	0	—	0.2207	10
	$\frac{1}{2}$	0.1388	0.2206	12
	$1\frac{1}{2}$	0.1455	0.2227	12
	3	0.1750	0.2208	16

\* Vulcanised to optimum crosslink density in an air oven at 100°C.

ical crosslinks. The reaction rate of the ZDC-TMTD system (D) decreases when a portion of ZDC is replaced with ZMBT in compound F.

As the prevulcanisation proceeds the viscosity of the latex compound increases and in all the compounds under study the viscosity variation is almost the same (Table III). The determination of viscosity at different periods of prevulcanisation under different shear rates shows that the flow behaviour of the latex compounds are little affected by prevulcanisation.

The polysulfidic content in the vulcanisates from latex compounds prevulcanised to different periods are given in Table IV. The V<sub>r</sub> values which are a measure of total crosslinks in the dried and vulcanisate films are also given in Table IV.

It can be seen that for samples A, B, C, D, E, and F, where there was no prevulcanisation, the percentage of polysulfidic linkages was lower. But in the case of the same samples which were prevulcanised for different periods at 70°C and later post-vulcanised at 100°C higher percentage of polysulfidic linkages was obtained. The percentage of polysulfidic linkages was higher as the extent of prevulcanisation increases even though the total crosslink concentration of the final vulcanisate is almost same irrespective of the extent of prevulcani-

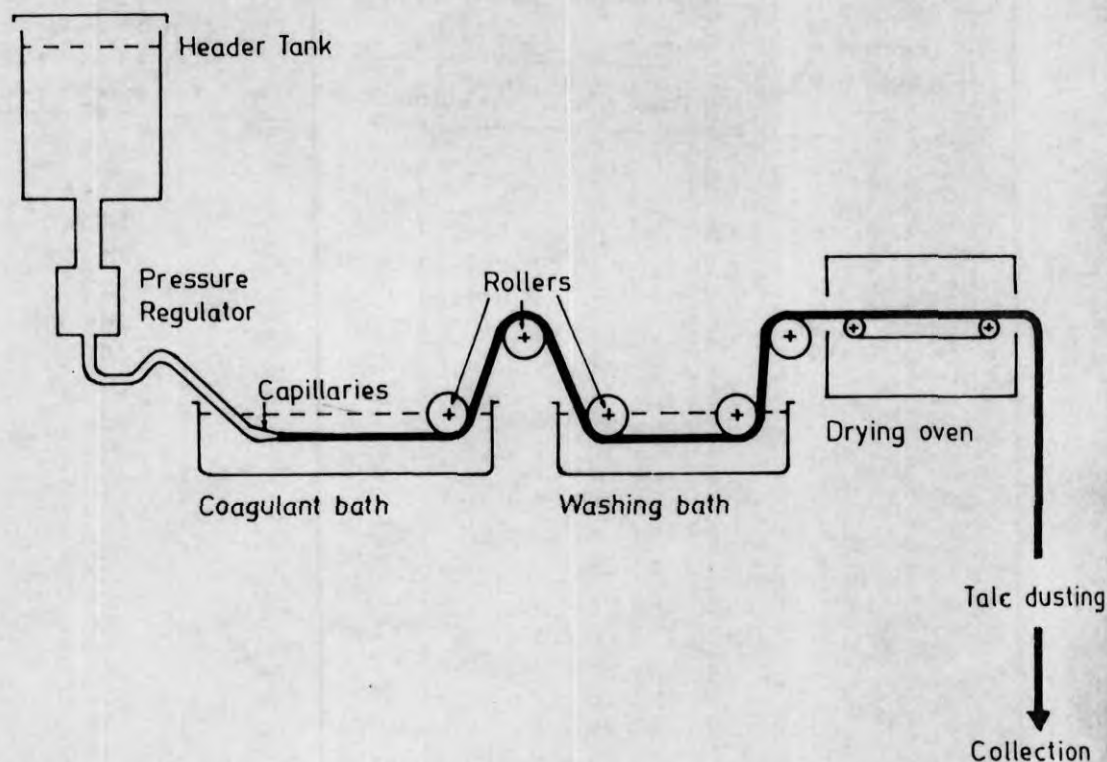


Fig. 3. Schematic diagram of latex thread production.

sation. It has been reported that in the vulcanisation of dry rubber as the vulcanisation temperature becomes lower, the chances for the formation of polysulfidic type linkages are high.<sup>11</sup> So the higher polysulfidic linkages in the prevulcanised latex films may be attributed to the low prevulcanisation temperature (70°C).

Test properties of the thread produced from latex compounds 'B' and 'F' are given in Tables V and VI. The prevulcanised latex compounds are found to be better in extrusion and subsequent processing with respect to more uniformity in count and comparative less tacky property. Tensile strength and modulus of the thread are improved only up to a certain extent of prevulcanisation (Table V) and above that level the properties decrease.<sup>6</sup> In the case of Compound B and F the ideal range of prevulcanisation time lies between half an hour and one and a half hours. The low tensile properties for the threads from latex compounds having higher extent of prevulcanisation (3 h duration) may be attributed to low inter-particle fusion. The tensile properties are not much improved after leaching and drying which can offer better inter-particle cohesion. One peculiarity with latex thread production is that a limited level of stretching at the wet gel stage occurs during the processing and this, in combination with low inter-particle cohesion of the wet gel may be a reason for this low tensile properties.

The aging resistance of the threads from prevulcanised latex compounds having 3 h heating time is found to be inferior to that for threads obtained from unvulcanised latex compounds and from latex compounds which were prevulcanised for shorter times (Table VI). This can be attributed to the higher poly sulphidic content in the threads heated for 3 h (Table IV).



TABLE V  
Physical Properties of Latex Threads

Compounds	Duration of prevulcanisation (hrs)	Modulus 300%, MPa		Tensile strength, MPa		Elongation at break %	
		Unaged	Aged*	% Retention	Unaged	Aged*	% Retention
B	0	1.40	1.30	92.8	16.5	14.0	84.8
	$\frac{1}{2}$	2.10	1.90	90.4	17.2	14.5	84.0
	$1\frac{1}{2}$	2.34	1.98	84.6	18.0	15.0	83.3
	3	1.85	1.34	72.4	12.87	6.81	52.9
	0	1.80	2.00	111.0	15.0	14.5	96.6
F	$\frac{1}{2}$	2.50	2.60	104.0	18.5	17.5	94.5
	$1\frac{1}{2}$	2.40	2.35	97.8	18.0	16.5	91.6
	3	2.12	1.68	79.2	14.29	9.5	66.0
						800	93.0
						790	91.0
						788	89.7
						641	76.6
						600	92.3
						710	88.7
						685	87.8
						600	80.0

\* Aged for 22 h at 100°C.

TABLE VI  
Effect of High Temperature Aging on the Properties of Threads (Heat Resistant Type)

Compound	Duration of prevulcanisation (hrs)	Modulus 300%, MPa		Tensile strength, MPa		Elongation at break %	
		Unaged	Aged*	% Retention	Unaged	Aged*	% Retention
F	0	1.80	1.45	80	15.0	7.8	52.0
	$\frac{1}{2}$	2.50	1.95	78	18.5	10.0	54.0
	$1\frac{1}{2}$	2.40	1.80	75	17.50	8.5	48.5
	3	2.12	1.38	65	14.29	5.14	36.0
						500	83.0
						600	81.8
						810	76.9
						780	66.6
						750	

\* Aged for 2 hours at 150°C.

The authors are grateful to Dr. A. P. Kuriakose, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-22 for his valuable suggestions and guidance in this work. The authors also express their gratitude to Shri. C. M. George, Project Officer, Department of Rubber Processing, Rubber Board, Kottayam-686009 for his permission and encouragement for undertaking this work.

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Received April 28, 1989

Accepted July 13, 1989