987 2

EFFECT OF VISCOSITY MODIFIERS ON PICK-UP AND PHYSICAL PROPERTIES OF DIPPED GOODS

By

K. T. MANI AND E. V. THOMAS
(Rubber Research Institute of India, Kottayam, India)

INTRODUCTION

A number of rubber products are manufactured from rubber latex using a simple technique called dipping, which in essence, is a process of immersing a former in a latex compound followed by withdrawal and drying. Viscosity of latex is a major factor deciding the thickness of the latex deposit. Control of viscosity is more important than that of concentration. A larger variation in deposit weight being obtained if the total solids are kept constant and viscosity varied than if the viscosity is kept constant and the total solids altered (Madge, 1933 — 34).

Viscosity of latex can be modified by the addition of certain chemicals which are usually called thickeners. Although several aspects of latex dipping have been studied (Madge, 1933 — 34 ; Sutton, 1957 ; Blackley and Gorton 1967 ; Gorton and Kuzmany, 1980) no systematic study on the comparative thickening efficiency of the chemicals has been reported. Gorton (1967) established relationship between dwell time, latex compound viscosity and deposit thickness for straight and coacervant dipping by variation in dwell time and compound viscosity and have been examined over a wide range of latex compounds (Gorton and Iyer, 1973).

This paper describes a study on the comparative thickening efficiency of five viscosity modifiers. Also the effect of dwell time and mode of dipping on pick-up and the effect of the thickeners on the physical properties of the vulcanizates have been studied.

EXPERIMENTAL

The base formulation adopted is given in Table III - 1. All insoluble solid ingredients were incorporated into the latex in the form of dispersion and insoluble liquid ingredients were added in the form of emulsion. To avoid web formation and zinc oxide thickening centrifuged latex was de-ammoniated to 0·2 percent ammonia before compounding. The latex compound was allowed to mature for 24 hours before adding thickener and another 24 hours after adding thickener at a temperature of 21·0 $\pm$ 0·5°C. After maturation care was taken to see that no air is drawn into the compound. Total solid content of the compound was determined before thickener addition. Thickener was added, taking steps to avoid dilution effect by adding suitable quantity of ammonia solution.

Proc. of the Intl Rubber Conference, 1984, Colombo, pp. 323-

Table III. 1. *Formulation of base latex compound**

Ingredient	Parts by weight dry (phr)	Parts by weight wet (phr)
NR Latex (as 60% HA concentrate)	100·00	167·00
Vulcastab VL, 20% solution**	0·25	1·25
Potassium hydroxide, 20% solution	0·30	1·50
Sulphur, 50% dispersion	1·00	2·00
Zinc oxide, 40% dispersion	0·25	0·63
ZDC, 50% dispersion	0·75	1·50
ZMBT, 40% dispersion	0·20	0·50
Nonox SP, 50% emulsion***	1·00	2·00

* Cure time at 100 ± 0·5°C = 50 minutes

** An ethylene oxide condensate preparation obtained from Alkali & Chemicals Corporation of India (ACCI) Ltd., Rishra.

*** A phenolic antioxidant obtained from ACCI Ltd., Rishra.

In this study, straight and wet — coacervant dipping (initial immersion in latex compound) were used with dwell times of ½ and 1 minute, coacervant being 10% formic acid. Test tubes (32 mm diameter) were used as formers, the dipping height being 12 cm. Temperature of the latex compound was maintained constant at 21·0 ± 0·5°C throughout the course of study. Pick-up is expressed as grams of dry deposit formed per square centimeter of the former.

Total solid content was determined as per BS — 1672 : 1972. Viscosity measurement was done using a Brookfield Viscometer (LVT Model) at 6 and 60 rev/min at 21·0 ± 0·5° C. All viscosity measurements were done just prior to dipping, also, precautions were taken to eliminate any thixotropic tendency of the compounds, by subjecting them to high shear stirring at 60 rev/min for 4 minutes before measuring the viscosity. For physical property determination, latex compound sheets were prepared according to the method described by Flint and Naunton (1935–36). Cure time was determined by 500% modulus and tensile strength determination. A series of sheets prepared by the above method were vulcanized at 100 ± 0·5°C for various times between 35 to 60 minutes. The sample with the maximum modulus and tensile strength was noted and the corresponding cure time was selected as the cure time of the compound. Tensile properties were determined by a Scott tensile testing machine as per ASTM Designation D : 412 — 75 using dumb-bell specimens cut with D - type die. Tear resistance was determined as per ASTM Designation D : 624 — 73. Ageing was carried out as per ASTM method D : 1870 — 68 using a tubular ageing oven at 70·0 ± 0·5°C for 96 hours.

RESULTS AND DISCUSSION

Effect on viscosity

The results, as given in Tables III.2 to III.6, show that among the five thickeners studied, the maximum thickening is caused by ammonium alginate and the minimum by cyclohexanol. The order in which the thickeners increase the viscosity of latices is as shown.

Cyclohexanol $<$ Casein $<$ Polyvinyl alcohol $<$ Sodium Carboxymethyl Cellulose $<$ Ammonium alginate.

This gradation is valid at all the concentration of the thickeners and at both speeds of the spindle. It is believed that the mechanism of viscosity increase is as described by Madge (1933 — 34).

Effect on pick-up

Cyclohexanol

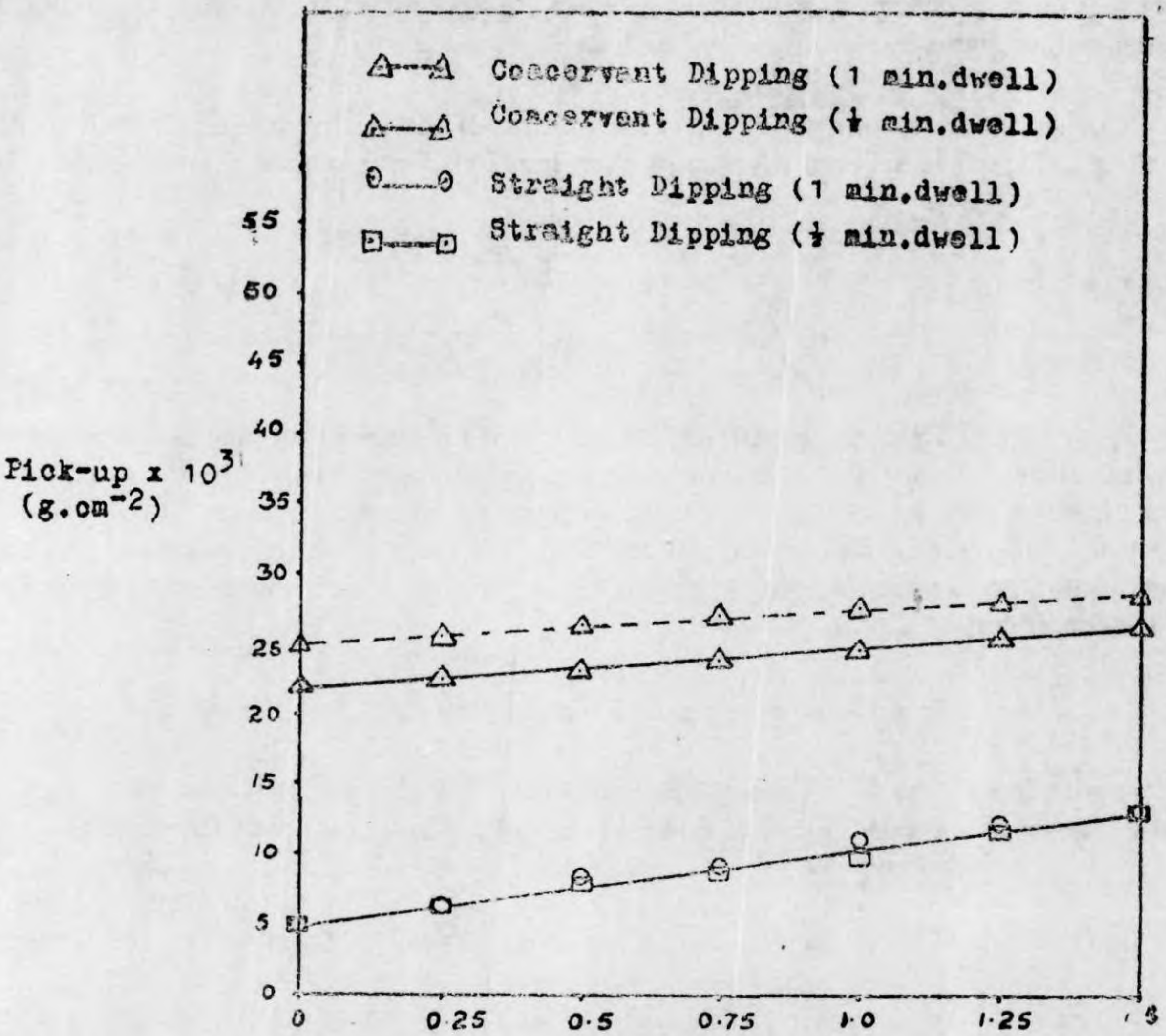
From Table III.2 and Figure III.1, it is seen that for straight dipping pick-up is independent of dwell time. For coacervant dipping pick-up is determined by the dwell time. In both cases, pick-up increases linearly with increase in concentration of cyclohexanol. The rate of increase in pick-up with concentration is more in straight dipping. At any concentration, coacervant dipping has got a higher pick-up ; this is more due to the action of the coacervant.

Table III.2. *Effect of cyclohexanol on viscosity and pick-up*

Concentration of thickener	Total solids content	Viscosity, Brookfield			Pick-up $\times 10^3$ (g. cm^{-2})			
		6 RPM	60 RPM	Spindle	Straight dipping		Coacervant dipping	
					½ Min Dwell	1 Min Dwell	½ Min Dwell	1 Min Dwell
(Phr)	(%)	(cp)	(cp)	No.				
0·00	55·4	100	57·5	2	5·1	5·1	22·0	25·0
0·25	55·6	115	60·0	2	6·6	6·6	22·5	25·6
0·50	55·7	120	62·5	2	8·0	8·3	23·0	26·3
0·75	55·8	130	70·0	2	8·8	9·0	23·3	27·0
1·00	55·9	150	75·0	2	9·8	11·1	24 6	27·6
1·25	56·1	175	90·0	2	11·8	11·9	25·4	28·2
1·50	56·2	240	108·5	2	13·3	13·6	26·2	28·4

Casein

Table III.3 and Fig. III.2 show that pick-up is practically independent of dwell time in straight dipping ; in coacervant dipping it is more dependent on dwell time. In both techniques, pick-up is linearly increasing with increase in casein concentration ; the rate of increase is more in coacervant dipping at both dwell times. Coacervant dipping has got more effect on pick-up than straight dipping.

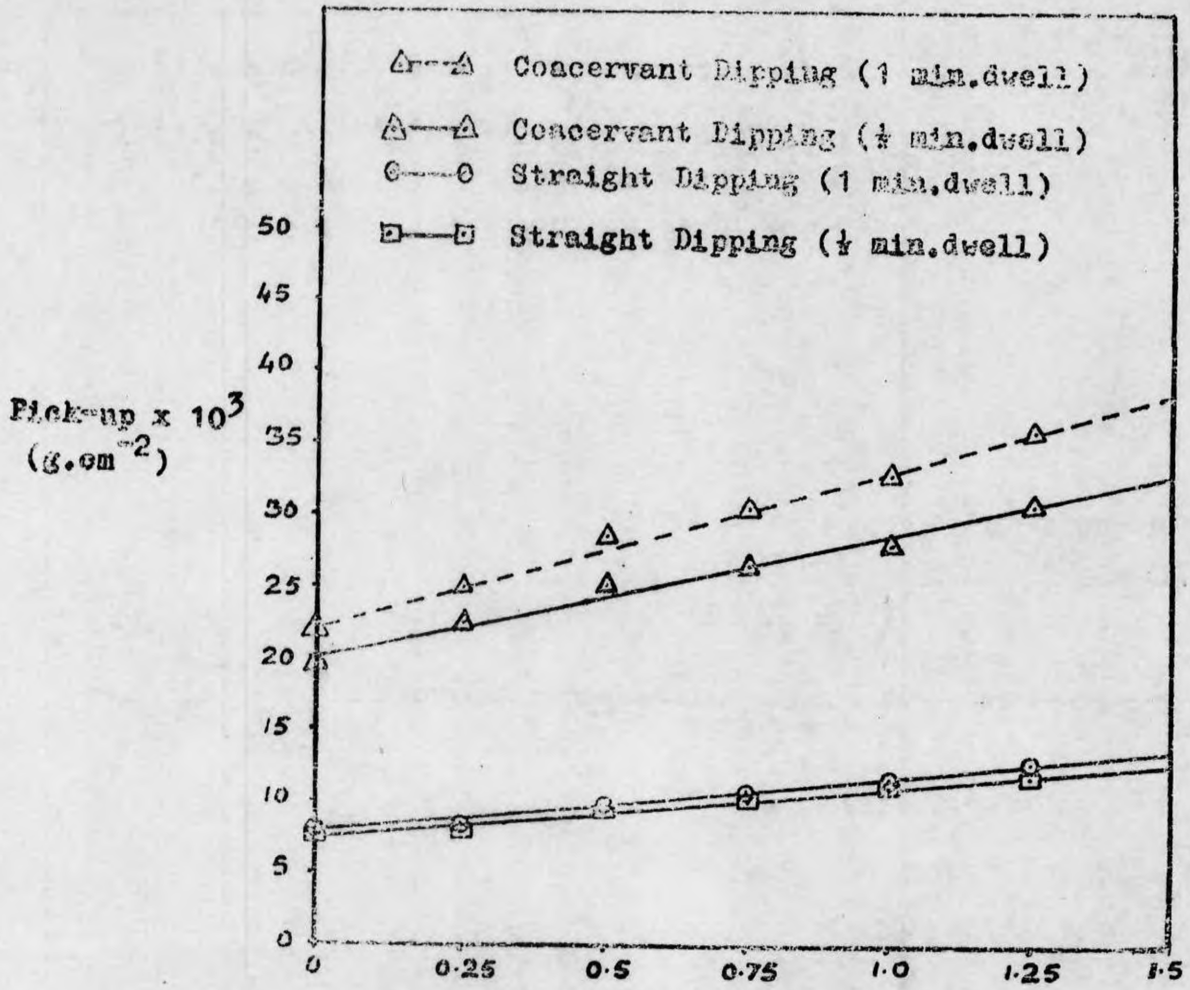


Concentration of Cyclohexanol (Phr)

Fig. III. 1. Effect of cyclohexanol on pick-up.

Table III.3. *Effect of casein on viscosity and pick-up*

Concentration of thickener (Phr)	Total solids content (%)	Viscosity, Brookfield 6 RPM (cp)	Viscosity, Brookfield 60 RPM (cp)	Spindle No.	Pick-up × 10³ (g. cm⁻²) Straight dipping ½ Min Dwell	Straight dipping 1 Min Dwell	Coacervant dipping ½ Min Dwell	Coacervant dipping 1 Min Dwell
0·00	55·4	240	120·0	2	7·6	8·0	19·3	22·0
0·25	55·6	265	127·5	2	7·8	8·3	22·5	25·0
0·50	55·7	290	147·5	2	9·2	9·8	25·2	28·4
0·75	55·8	330	167·5	2	10·0	10·8	26·7	30·4
1·00	55·9	375	186·5	2	10·9	11·6	27·9	32·8
1·25	56·1	450	215·0	2	11·8	12·7	30·7	35·7



Concentration of Casein (Phr)

Fig. III. 2. Effect of casein on pick-up.

Polyvinyl alcohol

From Table III.4 and Fig. III.3, it is evident that pick-up is only slightly enhanced by dwell time in straight dipping and dwell time has got only less effect on pick-up in coacervant dipping, when compared with cyclohexanol and casein. In both techniques pick-up is increasing with concentration, a linear increase is seen for both techniques. The rate of increase of pick-up is more in straight dipping. For coacervant dipping rate of pick-up increase is negligible upto 0·5 phr and afterwards increases slowly. Coacervant dipping has got more effect at lower concentrations.

Table III.4. *Effect of polyvinyl alcohol on viscosity and pick-up*

Concentration of thickener (Phr)	Total solids content (%)	Viscosity, Brookfield 6 RPM (cp)	60 RPM (cp)	Spindle No.	Pick-up × 10^8 (g. cm-²) Straight dipping ½ Min Dwell	1 Min Dwell	Coacervant dipping ½ Min Dwell	1 Min Dwell
0·00	55·4	250	115·0	2	6·4	7·4	20·6	22·3
0·25	55·6	600	202·5	2	8·7	10·1	20·9	21·8
0·50	55·7	1250	312·5	2	11·8	12·2	21·5	22·6
0·75	55·8	2050	445·0	2	14·7	15·5	22·5	23·7
1·00	55·9	3400	650·0	3	19·2	19·7	24·0	25·6
1·25	56·1	4900	880·0	3	21·6	21·6	25·3	26·7
1·50	56·2	6000	1050·0	3	23·4	23·6	26·8	28·5

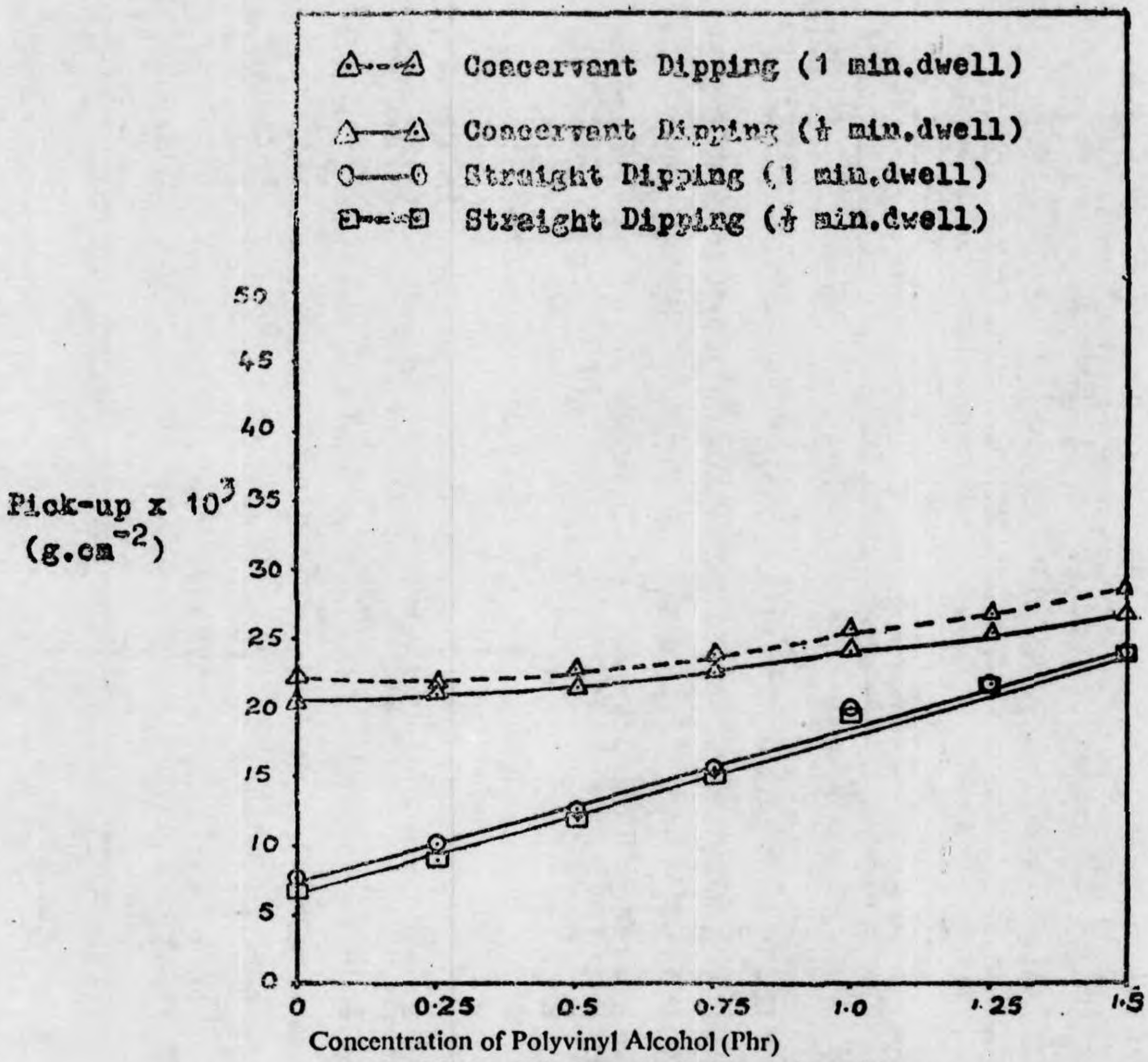


Fig. III. 3. Effect of polyvinyl alcohol on pick-up.

Sodium carboxymethyl cellulose

Table III. 5 and Fig. III. 4 depict that in straight dipping, pick-up is independent of dwell time ; dwell time has got more effect in coacervant dipping. In both techniques pick-up increases with concentration, but the relationship is non-linear. Rate of pick-up increase is more in straight dipping upto 1 phr ; beyond this concentration it is more for coacervant dipping. When the dwell time is half minute the coacervant dip gives lower pick-up compared to straight dipping. However, when the dwell time is raised to one minute, the coacervant dipping gives higher pick-up irrespective of the concentration of the thickener. It is to be assumed that sodium carboxymethyl cellulose retards the diffusion of the coacervant from the former surface to the latex compound.

Ammonium alginate

Pick-up is independent of dwell time in straight dipping and dependent in coacervant dipping as evident from Table III. 6 and Fig. III. 5. In both techniques pick-up non-linearly increases with increase in concentration ; rate of increase is more in coacervant dipping. For straight dipping the rate of increase decreases at higher concentrations. A higher pick-up is seen for coacervant method ; pick-up increases with increase in dwell time.

Table III.5. *Effect of sodium carboxymethyl cellulose on viscosity and pick-up*

Concentration of thickener (Phr)	Total solids content (%)	Viscosity, Brookfield 6 RPM (cp)	60 RPM (cp)	Spindle No.	Pick-up × 10^3 (g. cm^{-2}) Straight Dipping ½ Min Dwell	1 Min Dwell	Coacervant Dipping ½ Min Dwell	1 Min Dwell
0·00	55·4	150	70	3	6·1	7·3	18·7	19·7
0·25	55·6	3400	640	3	17·0	18·1	20·3	23·9
0·50	55·7	5900	1030	3	24·0	24·6	23·4	30·1
0·75	55·8	9000	1490	3	29·9	29·9	25·9....	31·8
1·00	55·9	18000	2950	4	31·1	31·3	30·5	41·9
1·25	56·1	22500	3700	4	35·3	35·9	38·0	43·6
1·60	56·2	35000	5750	4	38·0	39·0	57·7	59·9

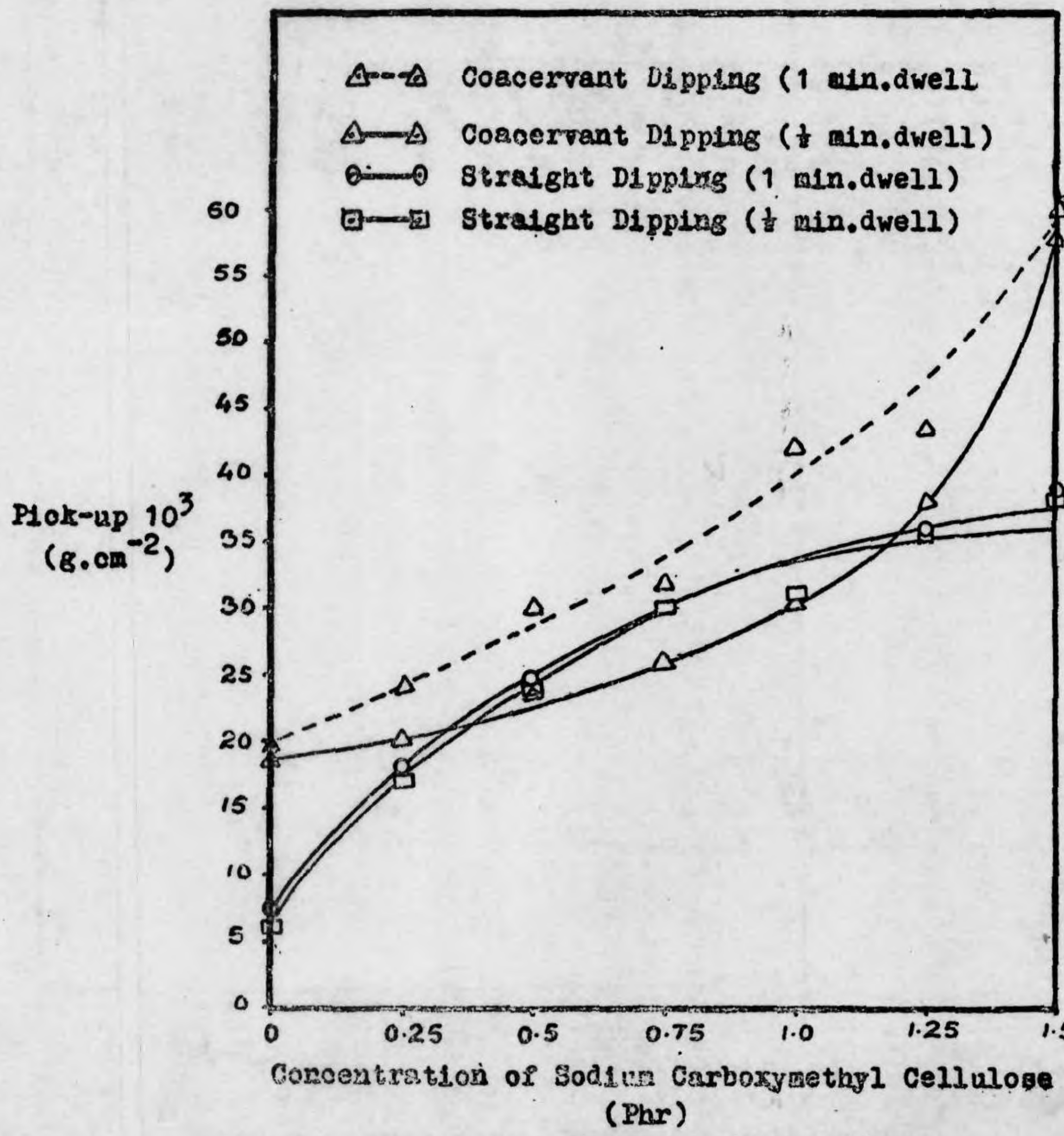


Fig. III. 4. Effect of sodium carboxymethyl cellulose on pick-up.

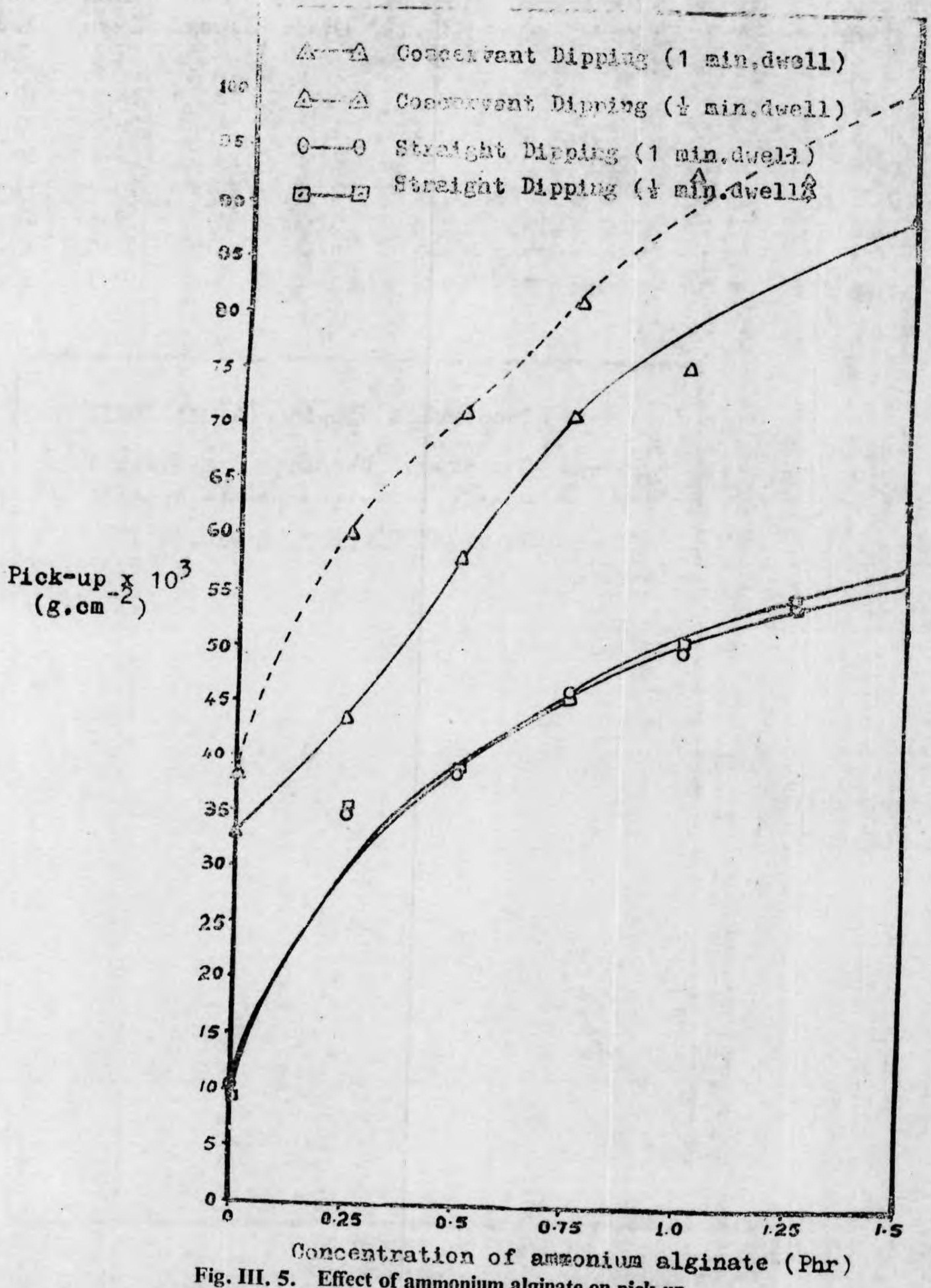


Fig. III. 5. Effect of ammonium alginate on pick-up.

Table III.6. *Effect of ammonium alginate on viscosity and pick-up*

Concentration of thickener (Phr)	Total solids content (%)	Viscosity, Brookfield 6 RPM (cp)	Viscosity, Brookfield 60 RPM (cp)	Spindle No.	Pick-up × 10^3 (g. cm^{-2}) Straight diping ½ Min Dwell	Straight diping 1 Min Dwell	Coacervant dipping ½ Min Dwell	Coacervant dipping 1 Min Dwell
0·00	55·5	350	152·5	2	9·6	10·5	32·9	38·2
0·25	55·6	5600	940·0	3	35·5	35·0	43·5	58·9
0·50	55·7	8500	1360·0	3	39·0	38·7	58·0	70·9
0·75	55·8	11900	1800·0	3	45·6	46·0	71·0	81·3
1·00	55·9	20000	3000·0	4	50·8	49·8	75·4	92·7
1·25	56·1	32000	4750·0	4	53·9	55·1	91·6	92·5
1·50	56·2	43500	6150·0	4	63·5	62·5	89·3	100·9

The results obtained from the present study are generally in agreement with the relationships established by Gorton and Iyer (1973).

Comparative evaluation

Straight dipping

The nature of the graph obtained by plotting pick-up of the latex compound against concentration of different thickeners may be seen in Figs. III. 6 and III. 7. It is clear from these that the dwell time has no influence on pick-up irrespective of the concentration of thickeners during straight dipping.

A linear increase in pick-up is observed for casein, cyclohexanol and polyvinyl alcohol with increase in concentration. The rate of increase of pick-up with concentration at both dwell times is in the order given below.

Ammonium alginate   Sodium carboxymethyl cellulose
Polyvinyl alcohol   Cyclohexanol   Casein.

For ammonium alginate and sodium carboxymethyl cellulose, the rate of increase of pick-up is more at lower concentrations than at higher ones. From the Figs. III. 6 and III. 7 the pick-up efficiency at any concentration and dwell time can be predicted.

Coacervant dipping

Based on pick-up the thickeners fall under the following order :

Polyvinyl alcohol ∠ Cyclohexanol ∠ Casein ∠ Sodium carboxymethyl cellulose ∠ Ammonium alginate

At lower concentrations pick-up efficiency of sodium carboxymethyl cellulose decreases and below 0·5 phr at ½ minute dwell it is having the least pick-up efficiency among the five thickeners ; but at 1 minute dwell this drawback gets reduced. A linear increase in pick-up with concentration is seen for cyclohexanol, casein and polyvinyl alcohol at both dwell times. The rate of increase in pick-up at both dwell times is in the order :

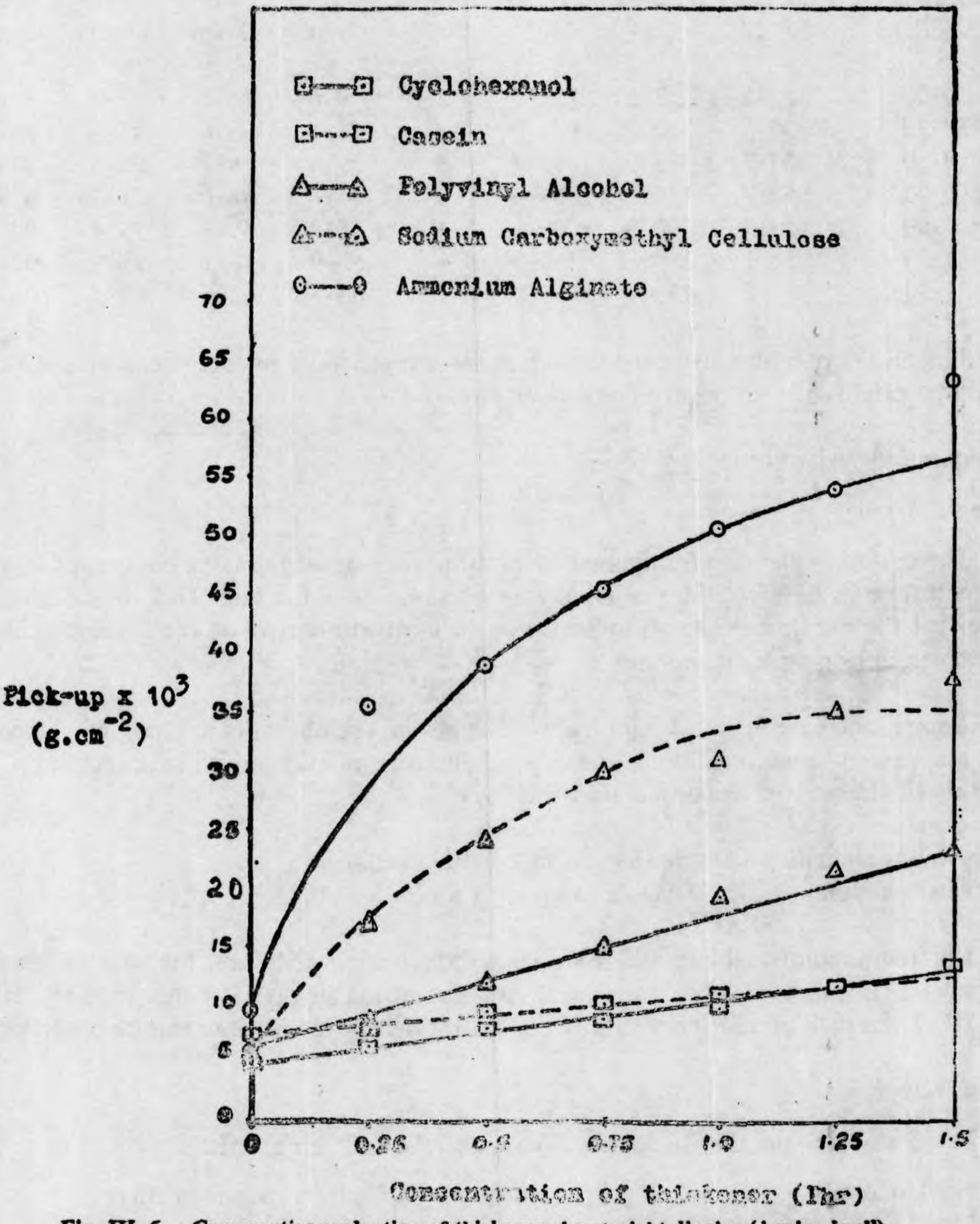


Fig. III. 6. Comparative evaluation of thickeners by straight dipping (½ min. dwell).