Indian Journal of Natural Rubber Research, **9**(1) : 22-27, 1996

USE OF SULPHURIC ACID AS COAGULANT FOR NATURAL RUBBER LATEX : LONG TERM EFFECTS ON RUBBER AND MACHINERY

Leelamma Varghese, K. Mariamma George and N. M. Mathew

Varghese, L., George, K.M. and Mathew, N.M. (1996). Use of sulphuric acid as coagulant for natural rubber latex : Long term effects on rubber and machinery. *Indian Journal of Natural Rubber Research*, 9(1) : 22-27.

Detailed investigations were carried out on the ageing behaviour of air dried sheet rubber prepared using sulphuric acid as coagulant, in comparison with that of sheets prepared using formic acid. Long term thermo-oxidative ageing of vulcanizates prepared from the sheets was also studied. Observations have also been made on the extent of corrosion on coagulation pans and sheeting rollers for a period of two years. It was found that decrease in the strength of raw rubber sheets prepared with sulphuric acid was negligible over a period of one year. Ageing behaviour of vulcanizates from sheets prepared using sulphuric acid was comparable to those prepared using formic acid, if the recommended conditions of use are followed. Corrosion of aluminium pans and sheeting rollers was negligible, when sulphuric acid was used as coagulant and recommended practices were followed.

Key words : Natural rubber, Latex coagulation, Sulphuric acid, Formic acid, Ageing, Vulcanizates.

Leelamma Varghese (for correspondence), K. Mariamma George and N. M. Mathew, Rubber Research Institute of India, Kottayam - 686 009, Kerala, India.

INTRODUCTION

Several attempts were made by earlier workers on the use of sulphuric acid as a coagulant for natural rubber (NR) latex for preparing sheet rubber (Wiltshire, 1932; Martin and Davey, 1934; Baker and Philpott, 1950; Best and Morell, 1955). However, its use has been very limited for various reasons such as its corrosive and non-volatile nature, difficulties in dilution and handling and the narrow price advantage over the more popular coagulant, formic acid. There has been a revival of interest on the use of sulphuric acid in recent years as there had been occasional instances of shortage in the supply of formic acid and significant price difference. Recent studies by George *et al.* (1992) indicated that sulphuric acid can be used as an effective and cheaper alternative to formic acid if factors such as dilution, dosage and washing of sheets and machinery are taken care of.

However, there are reports that the ageing behaviour of sulphuric acid coagulated rubber, as measured by tensile properties, is poor (Neef, 1950). Therefore, a detailed study was undertaken to investigate the storage/ageing behaviour of sheet rubber prepared using sulphuric acid. Observations were also made on the extent of corrosion of the aluminium pans and the sheeting rollers as a result of continuous use of sulphuric acid over a period of two years.

EXPERIMENTAL

Commercial grades of formic acid (85%) and sulphuric acid (99%) were used for the study. Fresh latex for the study was collected from the Rubber Research Institute of India Experiment Station. Sheet rubber was prepared under standard conditions, using varying concentrations of the acids and latex having different dry rubber content (DRC) levels (Table 1). The sheets were air dried at 60°C and raw rubber properties were determined as per IS:3660-1971. To assess the effect of coagulant on the rate of vulcanization and on the properties of vulcanizates, a gum rubber compound as per ACS 1 formulation and filled compounds containing HAF black and precipitated silica were prepared using a laboratory model two-roll mixing mill. The formulations of the mixes are given in Table 3. The cure characteristics were determined using a Monsanto Rheometer, R-100. The tensile properties were assessed using a Zwick Universal Testing Machine Model 1474 as per IS:3400-1977 (Part 1). Ageing of the vulcanizates was carried out at 70°C for different periods upto one month and the tensile properties after ageing determined. Room temperature ageing of the raw sheets was carried out by storing the sheets for a period of one year and determining tensile strength periodically. Specimens of size 40mm x 25mm x 3mm were cut from the sheets and the breaking loads determined using the Universal Testing Machine. The aluminium pans used for coagulation and the cast iron or mild steel sheeting rollers were observed periodically for a period of two years, for corrosion.

RESULTS AND DISCUSSION

Raw rubber properties of the sheets prepared under different conditions are given in Table 2. From the residual acidity values it was found that when standard conditions were followed as in Treatment 2, the residual acidity in sheets was almost identical to that in the case of formic acid, as indicated by the pH values of the water extract. It was observed that a slight retention of acid is possible if the quantity of acid used was more and/or if the sheets were not properly washed. Wallace plasticity (Po) and Mooney viscosity decreased with increased concentration of acid, as reported by Othman and Lye (1980). In the accelerated storage hardening test, Po was found to increase with increase in residual acidity. The results thus indicate the necessity for following standard conditions for coagulation of latex (George *et al.*, 1992).

Table 2. **Raw rubber properties**

Parameter	Treatments			
	1	2	3	4
Mooney viscosity (ML (1+4) 100°C)	90	84	76	69
Acetone extract (%)	3.2	3.2	3.4	3.6
Wallace plasticity (Po)	50	47	39	32
Plasticity retention index (PRI)	85	87	87	90
Accelerated storage hardening test (ΔPo)	18	21	23	28
Residual acidity (pH of aqueous extract)	5.72	5.71	5.06	4.96

The cure characteristics of ACS 1 compounds are shown in Table 4. Optimum cure and scorch times are higher than those of the standard sample (Treatment 1) and progressively increase with residual acidity. The tensile properties of the vulcanizates are almost identical irrespec-

Table 1. **Conditions of coagulation of latex to get 500 g dry sheet**

Treatment	Coagulant	Conditions
1	Formic acid	0.5%, 400 ml; 12.5% DRC; with washing
2	Sulphuric acid	0.5%, 300 ml; 12.5% DRC; with washing
3	Sulphuric acid	0.5%, 300 ml; 12.5% DRC; without washing
4	Sulphuric acid	5.0%, 50 ml; 20% DRC; without washing

Table 3. **Formulation of compounds**

Ingredient	ACS - I		HAF-filled		Silica-filled	
	A	B	A	B	A	B
Natural rubber	100	100	100	100	100	100
Zinc oxide	6.0	6.0	5.0	5.0	5.0	5.0
Stearic acid	0.5	0.5	2.0	2.0	2.0	2.0
HAF black (N 330)	-	-	40	40	-	-
Precipitated silica (insil VN3)	-	-	-	-	40	40
Naphthenic oil	-	-	4.0	4.0	4.0	4.0
Diethylene glycol	-	-	-	-	2.0	2.0
Antioxidant HS*	1.0	-	1.0	-	1.0	-
M B T	0.5	0.5	-	-	-	-
C B S	-	-	0.6	0.6	0.6	0.6
Sulphur	3.5	3.5	2.5	2.5	2.5	2.5

* 2,2,4-trimethyl 1,2-dihydroquinoline

Table 4. **Cure characteristics and vulcanizate properties of ACS-1 compounds**

Parameter	1 A	1 B	2 A	2 B	3 A	3 B	4 A	4 B
Optimum cure time at 150°C, min.	10.5	14.0	10.5	15.5	11.0	15.5	11.5	15.5
Cure rate index	11.1	9.1	12.0	9.1	11.7	8.3	11.7	8.0
Mooney scorch time at 120°C, min.	8.5	9.0	9.5	10.0	14.0	14.5	15.5	16.0
Hardness, Shore A	33	33	33	32	32	32	31	30
Tensile strength, N/mm^2	20.9	19.2	20.4	18.6	20.4	19.1	18.2	18.0
300% Modulus, N/mm^2	2.17	1.40	1.74	1.40	1.63	1.42	1.78	1.36
Elongation at break, %	1027	1076	1100	1040	1068	1031	1147	1020
Tear strength, N/m	41.3	33.5	40.6	32.6	37.4	32.7	37.9	32.8

A : with antioxidant B : without antioxidant

tive of the acid used for coagulation. Tensile strength was found to decrease slightly when the residual acidity was high as in the case of treatment 4.

Cure characteristics and tensile properties of the HAF filled compounds are given in Table 5. The increase in the cure and scorch times in the case of ACS 1 mix as a result of residual acidity was not observed in black-filled compounds, probably because of the neutralisation of the acids by carbon black which is known to be slightly alkaline. Tensile properties were comparable to those of the control sample. Cure characteristics and tensile properties of silica-filled compounds prepared using sulphuric acid coagulated sheets were also comparable with those of the control (Table 6).

Effect of ageing

The strength properties of raw sheets as determined by breaking load are given in Table 7. There was no observable change in the initial strength among the various treatments. The strength, however, decreased graudally during storage and after a period of one year the strength retained is about 96 per cent of the original value. The trend was almost identical for the control and the Treatments 2 and 3. However, the extent of degradation was noticeably higher in the case of Treatment 4, where the residual acidity was higher. Similar observations were reported by Best and Morrell (1955). According to their report only when the dosage of sulphuric acid was four times the normal dose, there was any noticeable difference in ageing resistance. However, use of such a high dosage is very much unlikely as the sole objective of using sulphuric acid is economy.

The degree of ageing of the vulcanizates is assessed by determining tensile properties. Figures 1, 2 and 3 show the percentage retention in tensile strength after ageing for 7, 15, 22 and 29 days. In the case of formic acid, tensile strength of the vulcanizates decreased during ageing, the rate of which slowed down after two weeks.

Table 5. **Cure characteristics and vulcanizate properties of HAF-filled compounds**

Parameter	1 A	1 B	2 A	2 B	3 A	3 B	4 A	4 B
Optimum cure time at 150°C, min.	13	15	13	15	14	15	13	15
Cure rate index	9.5	8	10	8.3	9.1	8.3	10	8.3
Mooney scorch time at 120°C, min.	14.5	14.5	15.0	15.0	16	16	17.5	17.5
Hardness, Shore A	50	52	49	48	49	48	48	48
Tensile strength, N/mm^2	25.5	26.0	27.2	25.4	26.8	27.9	28.7	26.6
300% Modulus, N/mm^2	7.6	7.2	6.9	6.7	6.8	7.3	7.2	6.9
Elongation at break, %	850	853	853	807	870	832	856	810
Tear strength, N/m	86	92	83	79	87	83	80	78

A : with antioxidant B : without antioxidant

When antioxidant was absent, the trend was similar, the absolute values being much lower. When sulphuric acid was used under standard conditions the initial drop in tensile strength was faster upto a period of two weeks, beyond which it slowed down significantly both in the presence and in the absence of antioxidant.

In the case of Treatment 3, where there was a slight residual acidity, tensile strength was found to decrease rapidly upto three weeks, after which it slowed down when antioxidant was available. The maximum extent of degradation was observed in the case of Treatment 4 where there was maximum residual acidity. Although antioxidant was found to improve the situation, the trend was almost identical.

Table 6. **Cure characteristics and vulcanizate properties of silica-filled compounds**

Parameter	1 A	1 B	2 A	2 B	3 A	3 B	4 A	4 B
Optimum cure time at 150°C, min.	16.5	17	19	20	20	21	16	17
Cure rate index	8	7.7	7.7	7.7	7.4	7.4	9.1	9.5
Mooney scorch time at 120°C, min.	29	28	30	32.5	30.5	32	30.5	36
Hardness, Shore A	53	52	52	51	52	51	52	51
300% Modulus, N/mm^2	3.8	3.9	3.2	3.4	3.0	3.1	3.5	3.5
Tensile strength, N/mm^2	26.6	26.2	27.4	25.9	26.9	25.1	27.0	26.7
Elongation at break, %	1095	1114	1169	1130	1140	1145	1142	1138
Tear strength, N/m	89	88	88	86	87	85	87	85

A : with antioxidant B : without antioxidant

Table 7. **Strength properties of raw sheets**

Period of storage (months)	Breaking load N/m			
	Treatment			
	1	2	3	4
0	31.2 (100.0)	31.5 (100.0)	31.0 (100.0)	31.1 (100.0)
3	30.7 (98.4)	31.5 (100.0)	30.7 (99.0)	29.8 (95.8)
6	30.4 (97.4)	30.7 (98.4)	30.4 (98.1)	29.0 (93.2)
9	30.5 (97.8)	30.6 (98.1)	30.2 (97.4)	29.0 (93.2)
12	30.0 (96.2)	30.0 (95.2)	30.0 (96.8)	28.7 (92.3)

Values in parentheses indicate percentage retention in strength

For the HAF black filled compounds, ageing behaviour of the control and Treatment 2, where sulphuric acid was used under standard conditions, were identical. However, in spite of the neutralising action of the black, residual acidity in the sheet as in the case of Treatment 4, caused a definite decrease in ageing resistance, although presence of antioxidant can improve the situation to a certain extent as is seen in Figure 2. In Figure 3 which shows the percentage retention in tensile strength

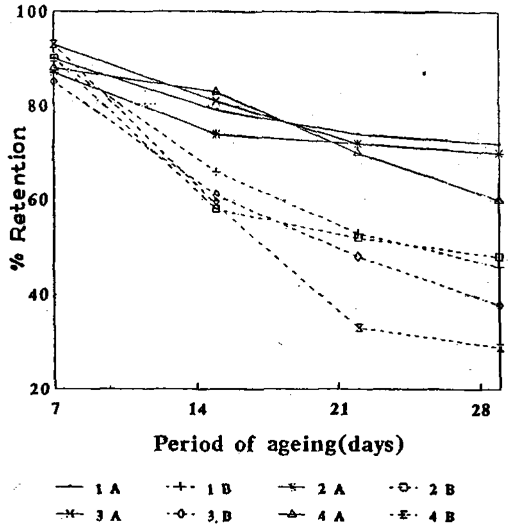

Fig. 1. Effect of ageing on tensile strength of ACS 1 vulcanizates

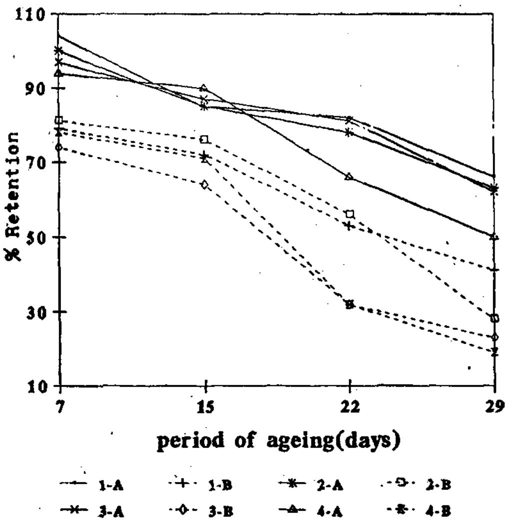

Fig. 2. Effect of ageing on tensile strength of HAF filled vulcanizates

of silica filled compounds, the best ageing characteristics was shown by the control. The sample prepared using sulphuric acid under standard conditions was found to be slightly inferior. However, Treatments 3 and 4, where residual acidity was higher, showed markedly inferior properties. Figures 4-6, which show the ageing resistance of the different vulcanizates in respect of retention in elongation at break, also support the above results.

Corrosion of sheeting rollers and aluminium pans

The replacement of formic or acetic acid by sulphuric acid for the coagulation of

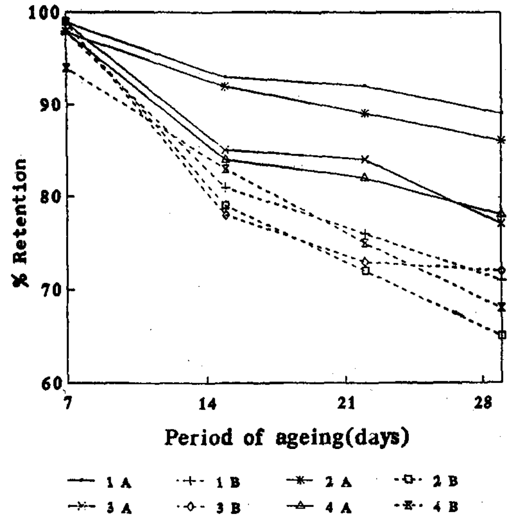

Fig. 3. Effect of ageing on tensile strength of silica-filled vulcanizates

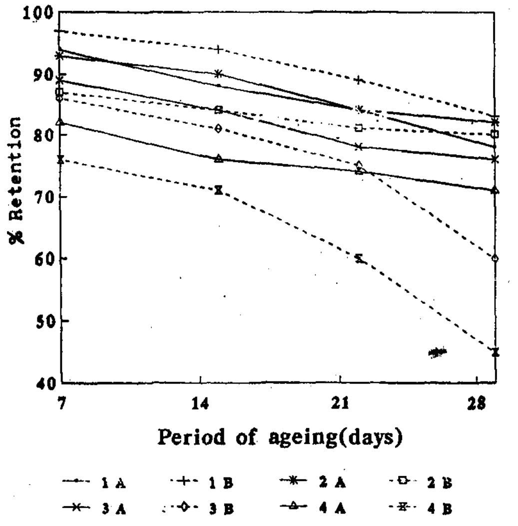

Fig. 4. Per cent retention of elongation at break of ACS 1 vulcanizates

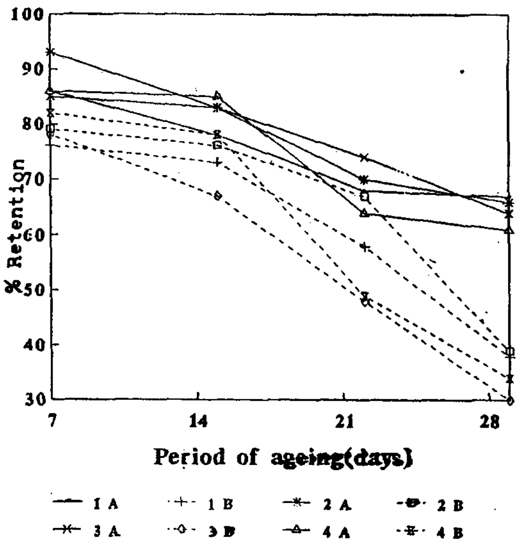

Fig. 5. Per cent retention of elongation at break of HAF-filled vulcanizates

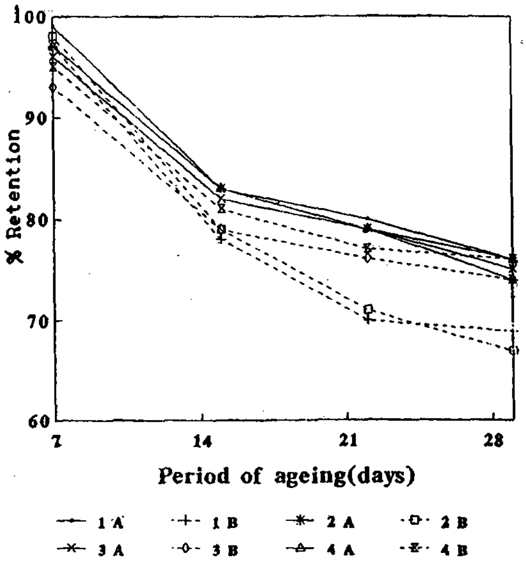

Fig. 6. Per cent retention in elongation at break of silica-filled vulcanizates

latex has the obvious attraction of cost saving. Such an economical factor ought to have prompted a widespread enthusiasm among planters for the use of sulphuric acid for sheet rubber production. But the actual tendency among planters have been to continue the use of formic or acetic acid as coagulants. The main reason for this has been attributed to the corrosive nature of sulphuric acid. It has been reported that if used in the minimum proportions, sulphuric acid contained in the serum will not cause any significant corrosion to the machines (Wiltshire, 1932). In the present work studies on the corrosion aspects, when sulphuric acid was used for making sheet rubber, were conducted for two years by making periodic visual observations. It was found that if sulphuric acid is used in the recommended conditions and if the pans and rollers are washed properly after sheeting, corrosion to the coagulation pans and sheeting rollers is negligible.

REFERENCES

Baker, H.C. and Philpott, M. W. (1950). Coagulation with sulphuric acid. *Journal of the Rubber Research Institute of Malaya*, **12** (Communication 269) : 265.

Best, L.L. and Morrell, S.H. (1955). Effect of sulphuric acid coagulation on properties of natural rubber. *Transactions of the Institution of the Rubber Industry*, **31**(3):133-140.

George, K.M., Varghese, L. and Mathew, N.M. (1990). Use of sulphuric acid as coagulant for natural rubber latex. *Journal of Plantation Crops*, ***20*** *(Suppliment) : 336 - 341.*

Martin, G. and Davey, W.S. (1934). Rubber from latex coagulated with sulphuric acid. *Journal of the Rubber Research Institute of Malaya*, **5** (3): 282-294.

Neef, De, J.C. (1950). Identification of rubber coagulated with too much sulphuric acid. *Journal of the Rubber Research Institute of Malaya*, **12**: (Communication 269) :263-264.

Othman, A.B. and Lye, C.B. (1980). Effect of pH of coagulation and sulphuric acid as a coagulant on natural rubber properties. *Journal of the Rubber Research Institute of Malaya*, 28(3):109-118.

Wiltshire, J.L. (1932). Sulphuric acid as latex coagulant. *Journal of the Rubber Research Institute of Malaysia*, 4(2):94-103.