

Quaternary Ammonium Surfactants as Alternative Coagulants of Skim Latex — A Laboratory Study

NG CHIEW SUM

Skim latex may be coagulated with sulphuric acid, formic acid or an electrolyte such as calcium chloride. Alternatively, if assisted by added molasses, it coagulates naturally. The cheapest and most popular coagulant is sulphuric acid. However, serum obtained tends to be too acidic and causes effluent problems. In the present study, two quaternary ammonium compounds are investigated as coagulants. Results show that they are effective under conditions normally encountered in practice. Age of latex, ammonia levels and the presence of carboxylate soap do not affect coagulation efficiency and yield. A less polluting serum effluent is obtained. Raw rubber and vulcanisate properties are examined and preliminary cost figures are given.

Skim latex is a by-product of latex concentrate production. Skim latex has a dry rubber content (d.r.c.) of 3% – 10% and represents about 8% of the dry rubber in the starting field latex. Conventionally, the rubber in the skim latex is recovered by coagulating with sulphuric acid, formic acid or an electrolyte such as calcium chloride. Coagulation may also be effected by adding molasses to the skim latex and allowing the bacteria to release acid from the molasses. This method is known as assisted biological coagulation (ABC)¹. The most popular coagulant is sulphuric acid (or spent acid) as it is the cheapest. After coagulation and processing, a serum essentially free of rubber but high in organic materials is discharged to waste. Recent legislation prompted by environmental considerations has compelled latex concentrate producers to treat the serum before it is discharged into the waterways. Various papers²⁻⁴ have discussed the content of skim serum and its treatment.

Sethu⁴ highlighted the problems of coagulation of skim latex with sulphuric acid. These include excessive sulphuric acid usage resulting in a low pH (<2.5) and high sulphate content in the serum (as high as 60 kg per tonne dry rubber processed). High sulphate level inhibits biological processes in the removal of organic materials from effluent⁵. To enable proper digestion of the organic materials in the highly acidic serum, a large amount of lime has to be added to neutralise and adjust to the right pH (ca. 7). Coagulation by formic acid produces serum with a lower sulphate level but it is more costly than sulphuric acid coagulation. Calcium chloride coagulation is seldom practised compared with acid coagulation. Resing⁶ has described the effects of various coagulating agents on the properties of skim rubber. He found that skim rubber obtained by microbial fermentation had good overall properties while coagulation by calcium

chloride led to poorer tensile strength and fatigue resistance under dynamic compression.

Thus it seems appropriate to investigate new methods or re-investigate some older methods of coagulation as alternatives to sulphuric acid or formic acid coagulation. This paper describes the coagulation of skim latex by surface-active quaternary ammonium compounds. Detailed studies on the effect of processing parameters such as ammonia level, d.r.c., age of skim latex and the presence of auxiliary chemicals on the efficiency of coagulation have been made. The raw and vulcanisate properties of the skim rubber are also described and compared with those of acid coagulated rubber. Preliminary costing is also given to assess the feasibility of this coagulation method.

EXPERIMENTAL

Source of Skim Latex

Skim latex was obtained in a laboratory centrifugal separator as a by-product of the centrifugation of field latex treated with 0.3% ammonia. The d.r.c. of the skim latex was 2% – 10%.

Chemicals

Gloquat C and Gloquat 1032 were obtained from ABM Chemicals as 50% aqueous solutions. The chemical structure of Gloquat C is 4-dodecyl-N, N, N-trimethyl benzenemethaminium chloride [CAS registry number 19014 – 05 – 2], $C_{12}H_{25} \cdot C_6H_4 \cdot CH_2 \cdot N(CH_3)_3 Cl$ and it has a molecular weight of 353.5. Gloquat 1032 is a quaternary compound of undisclosed chemical formula. Both chemicals were used without purification. Before use, the surfactant solutions were diluted to 2% or 5% with water and stirred well.

Determination of Dry Rubber Content

200 g of skim latex was coagulated with formic acid at pH 3–3.5. The

coagulum was allowed to consolidate overnight and then dewatered and creped on a laboratory creper. The weight of the rubber was noted after drying in a recirculating hot air chamber at 60°C for two to three days. Dry rubber content of the skim latex was calculated as a percentage of the skim latex weight. This method of d.r.c. determination differs from the standard method⁷.

Coagulation with Quaternary Ammonium Compounds

Coagulation of skim latex with quaternary ammonium compounds proceeds in a different manner from that of coagulation with an acid. Within 5 min of addition of quaternary ammonium compounds and with slight stirring to ensure uniform distribution, the skim latex flocculates and within 1 h it coalesces into a coherent coagulum. For practical usage, creping is best done after allowing the coagulum to consolidate for 2–4 hours.

Detection of Quaternary Ammonium Compounds in Serum

A standard method for the determination of quaternary ammonium compounds in milk⁸ was adopted with only slight modifications for detecting and quantitatively determining the amount of quaternary ammonium compounds in serum after coagulation of skim latex. The indicator bromophenol blue and enough hydrochloric acid solution (50%) were added to serum to render the serum solution acidic. This was followed by the addition of acetone in serum to precipitate residual rubber and non-rubber substances, leaving a clear solution of quaternary ammonium compounds in water/acetone. The acetone/water solution was filtered and the filtrate washed with a small volume of petroleum ether. The acetone was subsequently removed by evaporation on a water bath. The

quaternary ammonium compounds were extracted with portions of 1,2-dichloroethane. The dichloroethane layer was separated and shaken with 1% sodium carbonate solution. The presence of quaternary ammonium compounds in serum is indicated by the blue colour in the lower dichloroethane layer. (Figure 1).

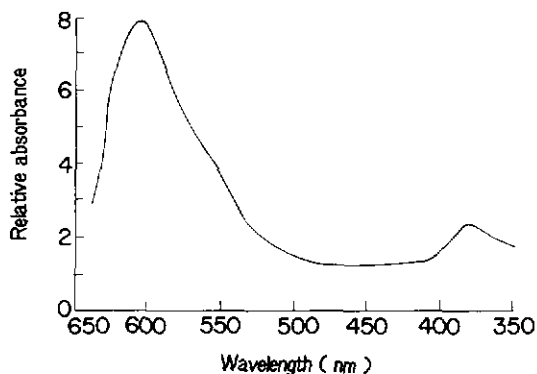


Figure 1. Ultraviolet visible light spectrum of bromophenol blue and quaternary ammonium compounds.

For quantitative determination, transmission of visible light was read at 606 nm in a Spectronic 20 (Bausch and Lomb) spectrophotometer. The transmission/concentration relation (Figure 2) obeys

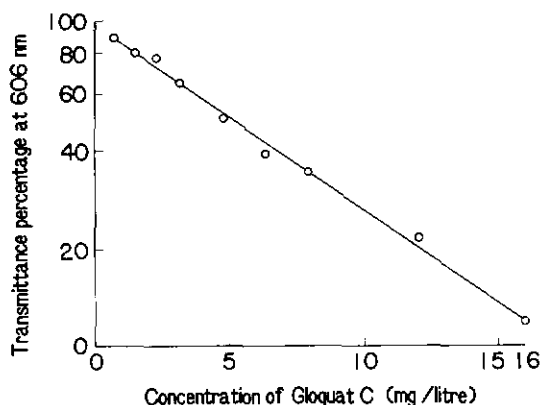


Figure 2. Plot of log transmittance versus concentration for Gloquat C.

the Lambert Beer Law for concentrations up to 16 mg per litre of a quaternary ammonium compound tested ($\lambda_{\max} = 606$, $\epsilon = 1.8 \times 10^4 \text{ mole}^{-1} \text{ l cm}^{-1}$).

Rubber Hydrocarbon

Rubber hydrocarbon was determined according to the relevant standard method⁹. In this method, the rubber is oxidised by a chromic acid digestion mixture (200 g of chromium trioxide in 500 ml of water and 150 ml of concentrated sulphuric acid). The acetic acid produced stoichiometrically is titrated with an alkali.

Raw Rubber and Technological Evaluations

Raw rubber properties were evaluated according to SMR test procedure¹⁰. Metallic contents were determined by a dry ashing and atomic absorption method¹¹. Rubber was compounded in an ACS 1 mix and in a sulphur/cyclohexyl benzyl sulphenamide (S/CBS) gum mix (Rubber 100, Sulphur 2.5, CBS 0.5, Stearic acid 1.5, ZnO 3.5 – the figures are parts by weight). Mooney scorch was measured on a Mooney viscometer and the cure characteristics were further tested on a Monsanto rheometer TM100. Tensile stress-strain properties were evaluated according to BS 903 for vulcanised rubber.

RESULTS AND DISCUSSION

Effect of Skim Latex pH

Skim latex of high ammonia level (pH 10.2) was deammoniated by a mechanical stirrer and a table fan and samples were withdrawn for coagulation. The rubber yield *vs* volume of chemical added at two different pH is shown in Figure 3. There appears to be a minimum concentration – the optimum concentration – at which all the rubber is coagulated leaving a clear serum and this optimum

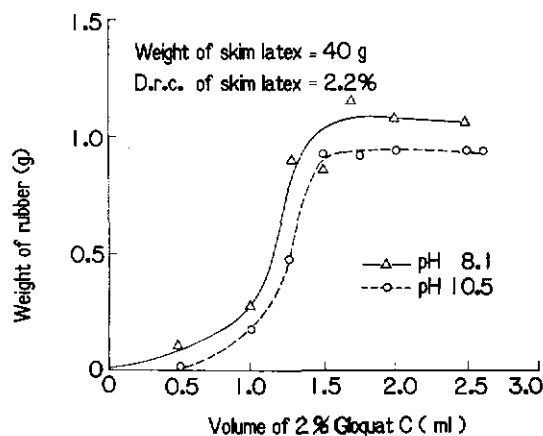


Figure 3. Effect of pH on coagulation of skim latex — plot of rubber yield versus volume of Gloquat.

concentration corresponds to the intersection point of two portions of the curve relating rubber yield and chemical added. Furthermore, it is independent of the pH of the skim latex and thus of ammonia level. This point is more clearly shown in Figure 4 which is replotted from data obtained from a series of yield *vs* chemical curves at various pH.

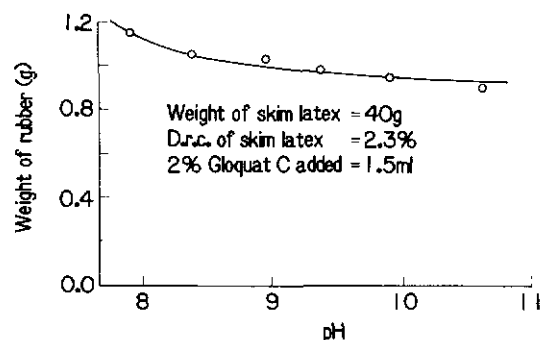


Figure 4. Effect of pH on coagulation of skim latex — plot of rubber yield versus pH.

Effect of Dry Rubber Content of Skim Latex

In normal practice, skim latex may be blended with washings from the centri-

fuge bowl or from latex discharging tanks. The latter may have lower dry rubber content than skim latex. This effect of dilution on coagulation was investigated. Skim latex of d.r.c. 6.8% was treated with Gloquat 1032 at various levels. Another batch was diluted to 3.9% d.r.c. with water and similarly treated. Results in Figure 5 shows that dilution of skim

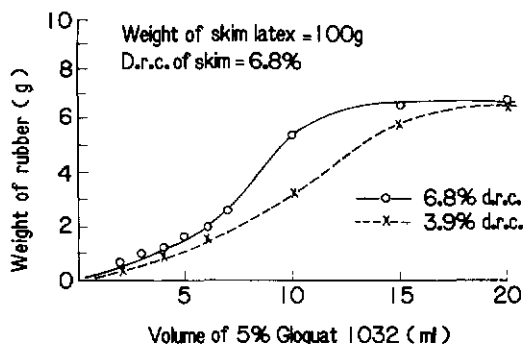


Figure 5. Effect of dry rubber content on coagulation of skim by surfactant.

latex does affect the coagulation efficiency of surface-active quaternary ammonium compounds in that it increases the optimum level of chemical used for complete coagulation.

Effect of Age of Latex

Skim latex forms only a small portion of rubber production in a latex concentrate factory. It may be necessary to accumulate skim latex over a period of three to seven days before coagulation in bulk. To examine this effect, skim latex samples were kept for various periods of time and coagulated with Gloquat 1032. Rubber weight and yield against various concentrations of surfactant are shown in Figure 6. Storing of skim latex over various periods does not affect the efficiency of coagulation.

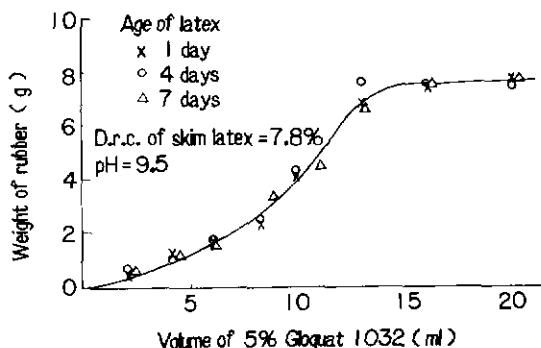


Figure 6. Effect of age of skim latex on coagulation by surfactant.

Effect of Carboxylate Soaps

For various reasons, ammonium or potassium carboxylate soaps are used to treat field latex prior to centrifugation. Commonly used soaps are oleate and laurate. These are anionic in nature and increase the overall charge of rubber latex particles. This factor was investigated using ammonium laurate as an example. The addition of ammonium laurate does not affect the coagulation efficiency of Gloquat 1032 despite its anionic nature (Figure 7).

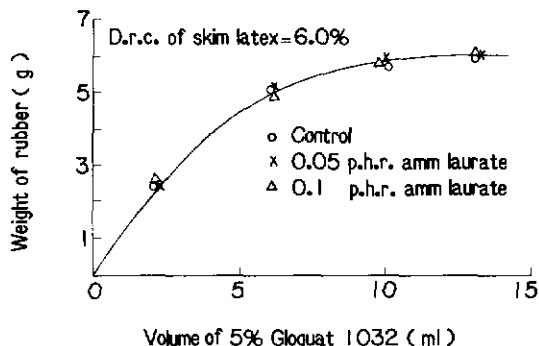


Figure 7. Effect of presence of carboxylate soap on coagulation of skim latex.

Comparison of Surfactant Coagulation and Acid Coagulation Methods

In the coagulation of skim latex with sulphuric acid or formic acid, the pH of

skim latex is reduced by the acidification. Coagulation sets in when the pH of the latex serum is decreased to around 4.0 or below (Figure 8). This reduction in serum

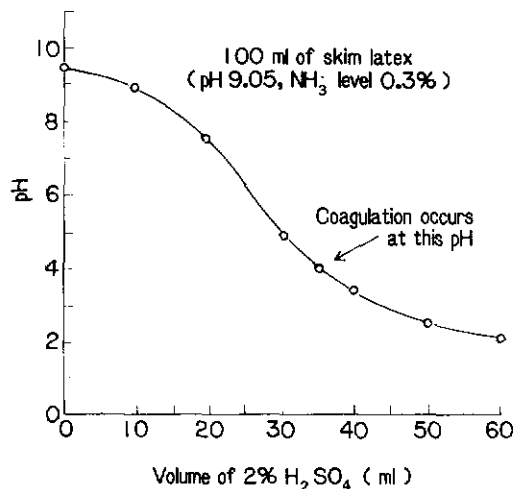


Figure 8. Acid coagulation of skim latex.

pH due to neutralisation by sulphuric acid or formic acid is accompanied by the simultaneous reduction of the surface negative charge on the latex particles. When the pH of the serum and latex particle surface falls below 4.0 – below the isoelectric point of proteins – latex destabilisation sets in.

Coagulation of skim latex with surface-active quaternary ammonium compounds may be contrasted with acid coagulation. The positive portion of the added quaternary ammonium compounds, represented by R_4N^+ where R_4 denotes four alkyl substituents (which may be different) on the nitrogen atom (N) is adsorbed on the latex particles. As the adsorbed positive charge neutralises the negative charge on the latex particles, coagulation sets in. Unlike with acid, coagulation with quaternary ammonium compounds does not

reduce the pH of the skim serum appreciably. The amount of quaternary ammonium compounds required, as stated earlier does not depend on the pH of skim latex. The amounts of Gloquat C and Gloquat 1032 required to coagulate skim latex produced on different days and from different sources, were found to be 3-5 p.h.r. and 7-10 p.h.r. respectively. For Gloquat C, this works out to be 8.5×10^{-5} to 14.1×10^{-5} mole per gramme skim rubber. Gloquat C is more efficient than Gloquat 1032 and merits further investigation as a coagulating agent on a bigger scale.

The specific action of surface-active quaternary ammonium compounds on the latex particles produces some direct consequences. Residual quaternary ammonium compounds in the skim serum is very small. Indeed, less than 2% of the added quaternary ammonium compounds goes into serum as determined by the absorptiometric method. The remaining 98% co-precipitates with rubber. In one experiment, when a fixed volume of skim latex was coagulated separately by quaternary ammonium compounds and acid, the apparent weight of rubber in skim latex obtained by quaternary ammonium compound coagulation was higher but its rubber hydrocarbon content was lower (Table 1).

Raw Rubber and Technological Properties

The raw rubber properties of skim rubber obtained by quaternary ammonium

compounds and acid coagulation are compared in Table 2.

The ash and nitrogen contents of all the three skim rubbers appear low compared with normal skim rubber. These may be caused by the high d.r.c. of the skim (ca 10%) from which these rubbers were derived.

The PRI of the four rubbers are in the increasing order: Gloquat C < Sulphuric acid < formic acid. Part of calcium and magnesium and other minor cations are strongly bound to the surface of the rubber particles as a slightly ionisable form with organic substances such as fatty acid soap and proteins which are themselves adsorbed by the rubber particles. When an acid is added in sufficient quantity to render the pH of the latex acidic, an ion-exchange reaction occurs; the hydrogen ion replacing the magnesium and calcium and other cations on the rubber surface. These metallic ions are then washed off in the serum. In quaternary ammonium compound coagulation, the weaker quaternary ammonium cation does not replace the metallic ions. As a result, ash content, of which the cations form a part, is higher in quaternary ammonium compounds coagulated skim rubber and PRI is lower due to the higher pro-oxidant metallic (copper, manganese and iron) content.

Technological Properties

Rheometer data obtained with ACS 1 formulation (Table 3) indicate that

TABLE 1. RUBBER AND RUBBER HYDROCARBON RECOVERED FROM SKIM LATEX

Coagulation method	Quaternary ammonium compound added (p.h.r.)	Wt of rubber (g)	Rubber hydrocarbon content (%)	Rubber hydrocarbon content \times Wt of rubber (g)
Formic acid	—	10.75	83.0	8.9
Gloquat C	4.7	11.04	78.9	8.7
Gloquat 1032	7.9	11.52	77.5	8.9

TABLE 2. RAW RUBBER PROPERTIES OF SKIM RUBBER COAGULATED BY QUATERNARY AMMONIUM COMPOUNDS AND ACID

Property	Coagulation method		
	Formic acid	Sulphuric acid	Gloquat C
P _o	57	50.5	54.5
PRI	73	66	46
N (%)	0.91	0.98	0.82
Ash (%)	0.22	0.25	0.28
Fe (p.p.m.)	4.2	4.9	6.1
K (%)	0.049	0.056	0.081
Mg (p.p.m.)	53	34	120
Ca (p.p.m.)	13	16	33
Mn (p.p.m.)	0.2	0.4	0.6
Cu (p.p.m.)	1.1	1.7	1.6
Total metal (%)	25.3	24.8	28.0
Ash			

Gloquat C coagulated skim rubber is more scorchy than acid-coagulated skim rubber. Cure rate is however unaffected. The state of cure is adequate and appear to be boosted by the residual quaternary ammonium compounds in skim rubber. It must be mentioned that quaternary ammonium compounds belong to a group of substances known to be rubber accelerators and which have been used previously to boost the curing rate of technically classified (TC) rubbers. These accelerators are commonly known as MOD-boosters and an example is Fixanol VR.

When compounded to a conventional CBS-accelerated sulphur gum mix formulation, the scorchiness of the quaternary ammonium compound skim rubber is again evident both in Mooney scorch and Monsanto scorch values (*Table 3*). However, it shows a slower cure rate than acid-coagulated skim rubber.

The remaining compounds from the rheometric measurements were press-cured at 140°C to optimum cure time and

tensile stress-strain results were obtained on punched dumbbell test pieces. All the skim rubber samples had adequate tensile strength and elongation at break although Gloquat C coagulated skim rubber had slightly lower elongation and tensile strength compared with the other two skim rubbers. Retention of tensile properties after ageing at 70°C for seven days was good.

Economics

It is well known that smallholders preserve latex with very high levels of ammonia, perhaps as high as 1.0% on latex weight, to keep latex fluid and its VFA low. Such practice would result in a very high pH of skim latex when the latex is centrifuged. Skim latex of high ammonia content may be deammoniated in a deammoniation tower or left in an open receptacle for a few days for the ammonia to evaporate. Nevertheless, for reasons peculiar to each factory, deammoniation may not be practised. Instead, a high level

TABLE 3. RHEOMETER DATA^a AND STRESS STRAIN PROPERTIES

Property	Coagulation method		
	Formic acid	Sulphuric acid	Gloquat C
Maximum torque T max (Nm)	2.62	2.64	3.05
Minimum torque T min (Nm)	0.58	0.63	0.71
T, Tmax-Tmin (Nm)	2.04	2.01	2.34
Optimum torque T ₉₀ (Nm)	2.42	2.44	2.81
Optimum cure time, t ₉₀ (min)	8.5	8.7	8.0
Scorch time, t ₂ (min)	1.3	1.3	0.8
Cure rate, t ₉₀ -t ₂ (min)	7.2	7.4	7.2
t ₂ (min)	4.8	6.9	1.8
t ₉₀ (min)	25.3	31.0	20.5
t ₉₀ -t ₂ (min)	20.5	24.1	28.7
Min. torque (Nm)	0.29	0.34	0.41
Max. torque (Nm)	2.69	2.54	2.58
Max. torque - min. torque (Nm)	2.40	2.20	2.17
Compound viscosity (ML 1 + 4, 100°C)	23.5	25.0	22.5
Max. viscosity (ML 1 + 4, 100°C)	39.0	42.5	34.0
Mooney scorch 120°C, T ₅	11.7	17.3	3.7
MR100 (MPa)	1.07	0.94	1.18
Tensile strength (MPa)	31.60 (99)	29.11 (101)	28.46 (103)
Elongation at break (%)	770 (94)	780 (94)	730 (97)
Modulus (MPa)			
300%	2.48 (157)	2.10 (159)	2.60 (128)
500%	6.87 (166)	5.28 (195)	8.31 (126)
700%	24.19 (124)	19.25 (144)	25.22 (110)

Figures within brackets denote retention of property after ageing at 70°C for seven days.

Tensile test pieces were press-cured at 140°C to optimum (Monsanto).

^aCompounded to ACS 1 formulation.

of sulphuric acid is added to skim latex to cause fast and complete coagulation, leaving an undesirably high level of sulphate in the skim effluent.

The direct chemical costs of coagulation are compared in Figure 9 and detailed

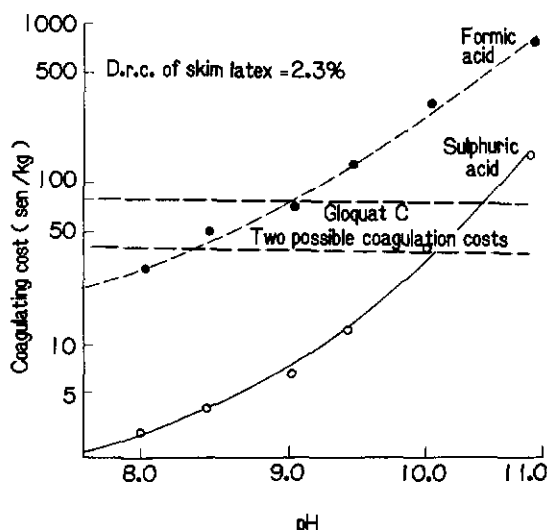


Figure 9. Economics of various coagulation methods.

calculations are shown in Appendix A. It is clear from the figures that Gloquat C is more attractive as a coagulating agent if the level of ammonia of skim latex (and thus its pH) is high. However, if coagulation is preceded by a deammoniation step and provided this can be done cheaply, coagulation with acid is more favourable economically. The above analysis must however be taken as preliminary. Since in this comparison, costs of deammoniation, liming and effluent treatment are not included.

CONCLUSION

Surfactant coagulation is an alternative method of skim coagulation. The coagulation efficiency is not adversely affected

by processing variables in the factory. It is less polluting than coagulation with sulphuric acid. It is more expensive than acid coagulation except when the ammonia level of the skim latex is high. Nevertheless, it opens up a new area of investigation for research on effluent treatment.

ACKNOWLEDGEMENT

The author wishes to thank Dr A. Subramaniam for helpful comments and suggestions in the preparation of the manuscript; Messrs David Graham, Jay Nambiar and Lau Chee Mun for helpful comments; Cik Norhanam bte Sulong, Messrs S. Puvanendran and Hau Eng Tion for technical assistance; the staff of Engineering and Testing Services Division and Specifications and Quality Control Division for analytical and technological tests.

Rubber Research Institute of Malaysia
Kuala Lumpur August 1982

REFERENCES

1. JOHN, C.K. AND PILLAI, N.M. (1971) Improvements to Assisted Biological Coagulation of Hevea Latex. *J. Rubb. Res. Inst. Malaysia*, 23(2), 138.
2. PONNIAH, C.D., JOHN, C.K. AND LEE, H. (1976) Treatment of Effluent from Block Rubber Factories. *Proc. Rubb. Res. Inst. Malaysia Ptrs' Conf. Kuala Lumpur 1974*, 310.
3. PONNIAH, C.D. (1976) Treatment of Acidified Skim Serum by a Laboratory Scale Oxidation Ditch. *Proc. Agro-ind. Wastes Symp. Kuala Lumpur 1975*, 94.
4. SETHU, S., CHANG, W.P., MOHD ZIN ABDUL KARIM, NORDIN BAKTI AND YONG, W.M. (1978) Effluent Discharge from Latex Concentrate Factories. *Proc. Rubb. Res. Inst. Malaysia Ptrs' Conf. Kuala Lumpur 1977*, 215.
5. NORDIN ABD. KADIR BAKTI AND CHANG WAI PONG (1976) Private Communication. Rubber Research Institute of Malaysia.

6. RESING, W.L. (1961) Observations on the Properties of Skim Rubbers *Proc. nat. Rubb. Res. Conf. Kuala Lumpur 1960*.
7. INTERNATIONAL STANDARDS ORGANISATION (1972) Natural Rubber Latex – Determination of Dry Rubber Content. *ISO 126-1972 (E)*.
8. ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (1975) *Official Methods of Analysis of the Association of Official Analytical Chemists*. Washington: Association of Official Analytical Chemists.
9. AMERICAN SOCIETY FOR TESTING MATERIALS (1980) Standard Methods for Rubber from Natural Sources – Chemical Analysis. Part 37: D1278-76. *1980 Annual Book of ASTM Standards*. Philadelphia: American Society for Testing Materials.
10. RUBBER RESEARCH INSTITUTE OF MALAYSIA (1973) RRIM Test Methods for Standard Malaysian Rubbers. *SMR Testing Bull. No. 7*.
11. NG S.K., HSIA, R.C.H. AND LAI, P.T. (1970) Spectrographic Determination of Calcium in Latex of *Hevea brasiliensis*. *Appl. Spectrosc.* **24**(6), 583.

APPENDIX A

ECONOMICS OF VARIOUS COAGULATION METHODS

pH	Sulphuric acid coagulation			Formic acid coagulation		
	Acid used (g)	Wt of rubber (g)	Coagulation cost ^a (sen/kg rubber)	Acid used (g)	Wt of rubber (g)	Coagulation cost ^a (sen/kg rubber)
7.9	0.045	1.08	2.8	0.16	1.18	29.7
8.35	0.06	0.99	4.1	0.25	1.03	53.1
8.95	0.10	0.97	7.0	0.33	0.98	73.7
9.35	0.18	0.94	13.0	0.58	0.96	132.2
9.9	0.63	0.93	45.0	1.43	0.92	340.0
10.6	2.25	0.86	178.0	3.41	0.90	828.0

$$^a \text{Coagulation cost (sen/kg)} = \text{Acid used} \times \frac{\text{Cost of acid (sen/kg)}}{1000} \times \frac{1000}{\text{Weight of rubber}}$$

Cost of formic acid = 219 sen/kg

Cost of sulphuric acid = 68 sen/kg

Gloquat C used 4 p.h.r., two price levels were assumed; \$5/kg of 50% solution and \$10/kg of 50% solution