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Studies on Some Anticoagulants and Preservatives of Hevea Latex

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Among a number of chemicals screened recently to find more suitable anticoagulants and preservatives for Hevea *latices three were promising. Sodium hypochlorite was found to be an effective anticoagulant, but as a short-term secondary preservative suitable only for field latex. Streptomycin sulphate was found to be an effective preservative for both field and concentrate latices. Tridimethyl aminomethyl phenol (DMP 30) preserves field latex well and when combined with ammonia, the mixture showed some synergestic effect. It was also found to be a good secondary preservative for latex concentrate.*

Field latex coagulates within a few hours of tapping, mainly due to the activity of bacteria, enzymes and divalent ions present in it. To prevent coagulation the usual practice is to add ammonia, formalin or sodium sulphite, their concentration depending on the period for which the latex is required to be kept fluid (COOK, 1960). All three have disadvantages. With ammonia, the most widely used anticoagulant, latex requires more acid for subsequent coagulation and, when used at high concentrations, it adversely affects drying time and imparts a dark brown colour to the rubber. Formalin is less effective, particularly in wet weather and with latices of certain clones. Sodium sulphite is not stable under tropical conditions and, when used in excess, may retard the drying of sheet, leading to its tackiness (RUBBER RESEARCH INSTITUTE OF MALAYA, 1966).

The commonest preservative for latex concentrate is again ammonia, used exclusively or together with a secondary preservative such as sodium pentachlorophenate, boric acid or zinc diethyldithiocarbamate (RUBBER RESEARCH INSTITUTE OF MALAYA, 1972).

ANGOVE AND PILLAI (1964 and 1965a and b) studied the use of various oxines (8-hydroxy quinoline), organozinc compounds, and rubber accelerators as secondary or tertiary preservatives or as both, with 0.2% ammonia as the primary preservative. However, it was found that most of these systems were either unsuitable or too expensive for commercial exploitation.

Screening of promising chemicals to find more suitable and cheaper anticoagulants and preservatives has therefore been continuing. This paper reports the results obtained with three of them: sodium hypochlorite (a powerful oxidising agent containing about 10% available chlorine), tridimethyl aminomethyl phenol (DMP 30) (a proprietary chemical from Rohm and Haas containing about 15% free phenol and about 60% bis-phenol) and streptomycin sulphate (a crude agricultural preparation).

EXPERIMENTAL

High ammonia latex concentrate was prepared by centrifuging one-day-old 0.3% ammoniated field latex and reammoniating the resulting concentrate to 0.7%. Low ammonia concentrate contained 0.2% ammonia and a secondary preservative. Latex concentrate samples were stored at 30°C in sterile bottles, or when large samples were

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required, in new 5-gal drums with anti-rust coating.

Sodium hypochlorite was used neat, but DMP 30 and streptomycin were added as a 10% aqueous solution on the basis of weight of latex.

The anticoagulant property of a chemical was estimated by the period for which it kept the field latex fluid, its short-term preservative effect was judged by its ability to prevent bacterial proliferation and formation of volatile fatty acids (VFA) and other degrading metabolites. A preservative for concentrate latex was selected on its ability as a bactericide, latex stabiliser and a rubber antidegradant for a period of six months.

Latex was tested for viable bacteria, by surface-plating 1-ml inocula from serial ten-fold dilutions using molasses/yeast extract agar (JOHN, 1968), incubating at 30°C for four days and counting the colonies by the method of JOHN AND TAYSUM (1963). It was tested for VFA number, mechanical stability time (MST) and potassium hydroxide number (KOH No.) according to prescribed methods (RUBBER RESEARCH INSTITUTE OF MALAYA, 1971). Discolouration of latex was observed after exposing it to bright sunlight continuously for five days. Samples for these tests were stored in sterile bottles (500 ml) without any air space inside, and a fresh bottle was used each time.

Testing of dry rubber for technological properties was carried out using rubber obtained from trials using 30-gal samples. Vulcanisate properties were tested using ACS I mix consisting 100 parts natural rubber, 5 parts zinc oxide, 0.5 part stearic acid, 0.5 part MBT and 3.5 parts sulphur.

RESULTS

Anticoagulants and Short-term Preservatives for Field Latex

Sodium hypochlorite. The field latex was treated with various levels of sodium hypochlorite and the bacterial population monitored with time to test its bactericidal effect *(Figure 1)*. Although concentrations up to 0.05% hardly had any effect on the bacterial population, higher concentrations were either bacteria-static or bactericidal.

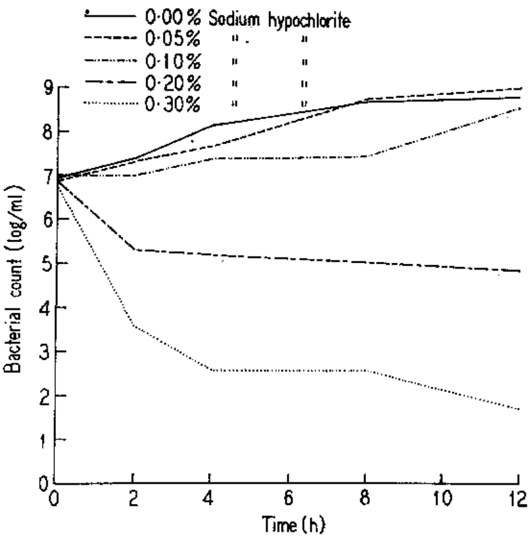

Figure 1. Bactericidal effect of sodium hypochlorite.

In normal latex, the anticoagulant property of sodium hypochlorite was similar to that of ammonia, 0.03, 0.05 and 0.1%, keeping the latex fluid for about 3, 6 and 12 h respectively. It was less effective than ammonia in latex collected on a rainy day, or that obtained from late tapping, or partially destabilised latex. Even 0.15% to 0.2% did not keep the abnormal latices fluid for long.

Field latex was treated with 0.03, 0.05, 0.10 and 0.2% sodium hypochlorite and allowed to mature for 1, 3, 5 and 20 h respectively to find out its effect on the alkalinity of latex and its subsequent coagulation. The pH of matured latex was then reduced to 5.2 using formic acid, and left to coagulate. A parallel experiment was carried out using ammoniated field latex. It was found that sodium hypochlorite up to 0.1% hardly affected the pH, and therefore consumed less acid to bring its pH to 5.2, compared to ammoniated field latex *(Table 1)*. However, it took a longer time to gel, particularly when the concentration was higher than 0.1%. Technological properties of rubbers obtained from latex treated with sodium hypochlorite were satisfactory compared to rubbers from ammoniated latex *(Table 2)*.

TABLE 1. CONSUMPTION OF 2% FORMIC ACID TO BRING pH TO 5.2

Preservative (%)	Maturation period (h)	pH after maturation	Acid used per 1000 g of latex (ml)
Ammonia			
0.03	1	6.88	55.0
0.05	3	7.53	75.0
0.10	5	8.94	136.0
0.20	20	9.40	239.0
Sodium hypochlorite			
0.03	1	6.40	37.0
0.05	3	6.22	35.0
0.10	5	6.33	42.0
0.20	20	6.49	65.0

TABLE 2. TECHNOLOGICAL PROPERTIES OF RUBBER OBTAINED FROM LATICES TREATED WITH SODIUM HYPOCHLORITE OR AMMONIA

Property	Ammonia (%)		Sodium hypochlorite (%)		
	0.03	0.10	0.03	0.05	0.10
Raw rubber					
Mooney VR	77	78	75	73	75
Mooney VC	56	55	55	53	54
T.C. strain (%)	72	81	72	78	68
PRI	95	89	91	86	69
Vulcanisate					
Cure time 40′/140°C					
Tensile strength (Kg/cm^2)	232	235	250	245	237
Aged 1d/100°C	149	143	139	156	106
Elongation at break (%)	750	785	750	800	750
1d/100°C	620	610	640	640	630
Modulus at 300 (Kg/cm^2)	16	15	17	15	16
1d/100°C	19	20	17	17	16

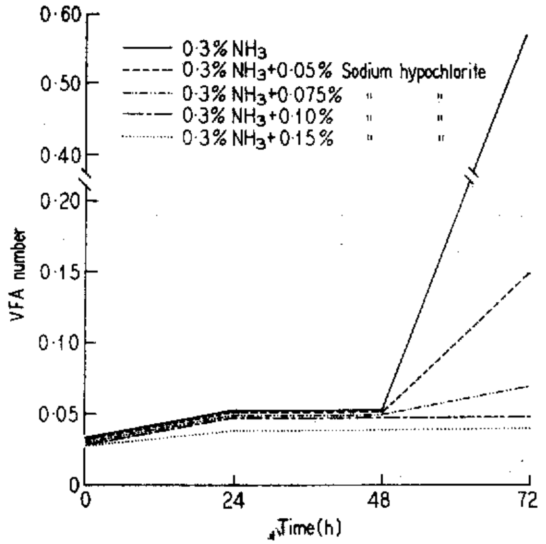

Figure 2. Effect of sodium hypochlorite on VFA build-up of field latex.

Sodium hypochlorite is an effective short-term secondary preservative, 0.1% preventing any VFA formation in ammoniated field latex *(Figure 2)*.

Streptomycin sulphate. Samples of field latex containing 0.3% ammonia were treated with various levels (0.005% to 0.1%) of streptomycin sulphate and tested for bacterial population at various intervals of storage to find out its bactericidal property. The bacterial population dropped from log 6.63 to 4.17 per millilitre in 44 h when treated with 0.01% and to log 2.04 with 0.1%. It also effectively controlled the VFA build-up in latex; with 0.05% there was hardly any increase in VFA over a period of three days *(Figure 3)*.

DMP–30. Ammoniated field latex was treated with various levels of DMP and tested after 48 h to find out its suitability as a short-term preservative. It was found that a combination of 0.1% ammonia and 0.1% DMP was as effective as 0.5% ammonia alone or 0.3% DMP alone in controlling the bacterial proliferation and VFA build-up, and that by increasing the level of ammonia to 0.2% DMP concentration can be halved *(Table 3)*.

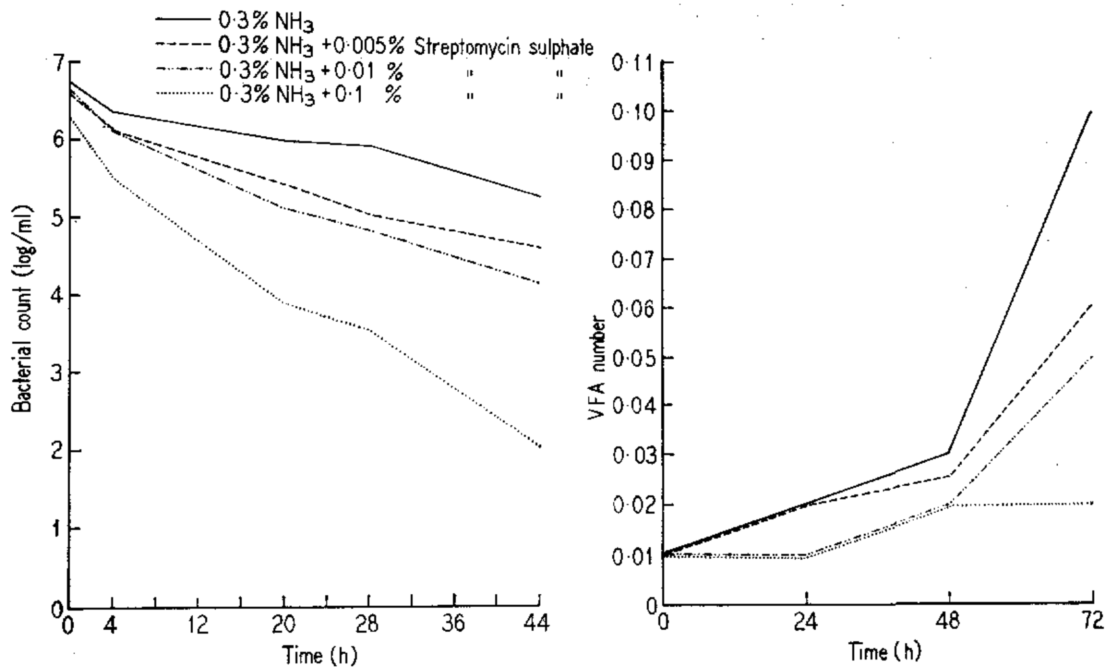

Figure 3. Effect of streptomycin sulphate on bacterial population and VFA of field latex.

TABLE 3. COMBINED PRESERVATIVE EFFECT OF DMP-30 AND AMMONIA

NH_3 (%)	DMP (%)	pH immediately after additions	Latex property after 48 h storage			
			pH	VFA No.	Bacterial count (log/ml)	Odour
0.10	0.05	9.18	8.53	0.23	8.15	smelly
0.10	0.10	9.25	9.25	0.03	5.85	no smell
0.10	0.15	9.30	9.30	0.03	5.66	no smell
Nil	0.30	8.85	8.50	0.03	5.43	slightly smelly
0.20	0.05	9.55	9.62	0.03	5.11	no smell
0.20	0.10	9.59	9.58	0.03	5.08	no smell
0.5	Nil	10.00	10.00	0.03	5.76	no smell

Secondary Preservatives for Concentrate Latex

Sodium hypochlorite. Concentrate latex ammoniated to 0.2% was treated with sodium hypochlorite up to 1.0% and tested at various intervals. In most trials 0.5% effectively controlled VFA, but in some even 1.0% was not effective. Even when VFA was effectively controlled, MST was adversely affected, the latex not responding even to the addition of lauric acid. The latex when exposed to sunlight had a grayish colour.

Streptomycin sulphate. Concentrate latex containing 0.2% ammonia was treated with various levels of streptomycin sulphate (0.02, 0.03, 0.04, 0.05 and 0.06%) but only at 0.04% to 0.06% satisfactory preservation was achieved for up to six months. MST values were rather poor but could be rectified by the addition of 0.03% lauric acid *(Table 4)*. There was no discoloration of latex even after severe exposure to bright sunlight.

DMP-30. Concentrate latex containing 0.2% ammonia was treated with various levels of DMP and tested at various intervals up to six months *(Table 5)*. Although 0.2% DMP preserved latex only for about a month, 0.25% prolonged the period to six months. By increasing the concentration to 0.3% a concentrate with slightly better properties resulted, but further increase did not produce better results. Satisfactory mechanical stability was obtained without the addition of lauric acid, the six-month-old latex giving an MST value of about 990 s compared to 1000 s for the HA latex. No discoloration of latex was observed even after its severe exposure to sunlight.

DISCUSSION

An ideal anticoagulant or preservative should function as a bactericide, enzyme poison and a metal chelating agent; in the case of latex concentrate, it should also provide adequate stability to latex. In addition, the chemicals should not adversely affect the processability of latex or the properties of the final product.

Sodium hypochlorite as an anticoagulant is about as effective as ammonia in normal field latex, about 0.1% keeping it fluid for about 8 h, but it is markedly less effective in abnormal latices. As it does not make the latex unduly alkaline, extra acid is not required for coagulation. Further, it has no marked deleterious effect on the properties of the resulting dry rubber. It is very effective as a short-term secondary preservative for field latex; with 0.3% ammonia and 0.075% sodium hypochlorite no VFA

TABLE 4. PROPERTIES OF STREPTOMYCIN SULPHATE (SS) TREATED LOW AMMONIA LATEX

Preservative system[a]	Age of latex (month)	Property			
		Bacterial count (log/ml)	VFA No.	KOH No.	MST (s)
0.7% NH_3 (Control)	0	2.51	0.01	0.41	60
	2	Nil	0.01	0.59	800
	3	Nil	0.01	0.63	765
	6	Nil	0.01	0.62	860
0.2% NH_3 + 0.02% SS	0	3.39	0.01	–	40
	2	6.98	0.35	0.99	275
	3	Nil	0.35	1.06	420
0.2% NH_3 + 0.04% SS	0	2.18	0.01	0.47	50
	2	Nil	0.07	0.75	720
	3	Nil	0.07	0.76	800
	6	Nil	0.07	0.82	900
0.2% NH_3 + 0.06% SS	0	1.85	0.01	0.48	50
	2	Nil	0.05	0.73	890
	3	Nil	0.05	0.98	925
	6	Nil	0.06	0.93	1 005

[a]All samples except the control contained 0.03% lauric acid.

build-up was observed for three days. To obtain similar effect with ammonia alone, between 0.5% and 0.7% is needed. When it is used as a short-term preservative for field latex, used for concentration products, part of it may be carried into the concentrate latex. It is unsuitable as a secondary preservative for concentrate latex because of its adverse effect on the properties of the resulting concentrate.

Sodium hypochlorite costs only 45 ct (M) per kilo. Its combined use with ammonia should therefore be acceptable as anticoagulant and short-term preservative. Its main drawback, however, is its instability, especially in tropical conditions of storage when its shelf life is reduced to about four weeks. The decomposition can be minimised if it is kept in vented containers in a cool dark place.

Streptomycin sulphate has been found to be an effective short-term secondary preservative for field latex, with 0.05% effectively controlling the VFA build-up in 0.3% ammoniated latex. It is also an effective secondary preservative for concentrate latex, with about 0.05% satisfactorily preserving the low ammonia latex at least for six months, the MST rectified by the addition of 0.03% lauric acid. Despite the high alkaline condition of the latex, no indication of the degradation of streptomycin was observed in the present investigation. Although the streptomycin used in the

TABLE 5. PROPERTIES OF DMP-TREATED LOW AMMONIA LATEX

Treatment	Age of concentrate (month)	pH	VFA No.	MST (s)	KOH No.	Bacterial count (log/ml)
0.7% NH_3 (Control)	0	10.58	0.01	65	0.35	2.6
	1	10.43	0.01	687	0.51	2.13
	3	10.22	0.01	823	0.53	1.4
	6	10.33	0.02	999	0.53	1.6
0.2% NH_3 + 0.2% DMP	0	10.08	0.01	35	0.39	2.5
	1	9.74	0.04	453	0.62	2.3
	2	9.64	0.11	482	0.70	1.9
	3	9.53	0.13	482	0.81	1.9
	6	9.40	0.10	595	0.78	2.2
0.2% NH_3 + 0.25% DMP	0	10.08	0.01	37	0.36	2.5
	1	9.90	0.02	698	0.54	2.2
	3	9.63	0.03	818	0.58	2.1
	6	9.51	0.04	823	0.65	2.2
0.2% NH_3 + 0.3% DMP	0	10.14	0.01	37	0.35	2.5
	1	9.93	0.02	782	0.49	2.3
	3	9.61	0.02	872	0.61	2.1
	6	9.51	0.02	985	0.58	2.0

investigation is the crude type, it is still quite expensive and its cost may be detrimental to its large-scale commercial use.

DMP 30 has been found to preserve the field latex well, a combination of 0.1% ammonia and 0.1% DMP or, 0.2% ammonia and 0.05% DMP being as effective as 0.5% ammonia alone or 0.3% DMP alone. A combination of ammonia and DMP is better than high levels of ammonia or DMP alone. It is also a good secondary preservative for latex concentrate at 0.25%. The present results thus confirm the earlier findings of RESING (1958) who has reported that DMP with ammonia can control bacterial degradation of field and concentrate latices and that the vulcanised latex film has good mechanical properties. Large-scale preparations of these latices are being investigated to further establish the effect of these chemicals on the properties of the resulting latex and dry rubber.

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