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COAGULATION OF NATURAL RUBBER LATEX WITH HYDROCHLORIC ACID (HCl)

BY

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SUMMARY

Natural rubber derived from HCl coagulation was tested for any deleterious effects, principally ageing, and it was found that under controlled conditions HCl coagulated rubber behaved better than formic acid coagulated rubber after shelf ageing as well as accelerated ageing.

INTRODUCTION

The writers in the early literature (Van de Bie, 1946; Wiltshire, 1932) did not consider HCl as an attractive proposition for the coagulation of natural rubber latex and there are references to inferior quality of the product: (1) a tendency to tackiness (2) undesirable side reactions (3) possibility of adverse effects on vulcanising behaviour and lack of attraction cost wise. Their reasons are not stated concisely and it was thought necessary that a fresh evaluation of rubber prepared by HCl coagulation would be useful, for the following reasons :—

(1) HCl is a raw material which is available locally

(2) Formic Acid, the preferred coagulant, can be in short supply

(3) No work has been done by the Rubber Research Institute of Sri Lanka to confirm the views expressed by other sources.

MATERIALS AND METHODS

HCl used in our experiments was the commercial acid (33-35% w/v), obtainable from Paranthan Chemicals Corporation, Sri Lanka. This acid is packed in 45 l capacity polythene cans, and the approximate nett weight of acid contained in a 45 l can is 51.7 kg.

Dilution of HCl

The concentrated acid (33-35% w/v) is far too corrosive and irritating since it fumes owing to the high volatility of the hydrochloric acid gas, thus rendering it practically impossibe to be handled in ordinary use without adequate safety measures. Therefore, it was necessary to try out varying dilutions of the acid so as to ascertain the highest concentration, which could be conveniently used without hazards and this was found to be around 20-25% (w/v) at which concentration there is no unbearable fuming. It is also recommended that the manufacturers of the acid should supply it at this concentration from which the consumer can make stock solutions of say 5% (w/v) to be kept readily available for use in coagulation. The 5% acid solution has to be diluted tenfold prior to use.

Acid treatment and preparation of coagulum

Several portions, of 50 ml each, were taken from a batch of fresh field latex and mixed separately with coagulant additives (0.5% hydrochloric acid, 1% formic acid, 2% acetic acid) and the resultant coagula were creped and dried in the usual way. The pH of the latex an each case was recorded immediately after mixing with the coagulant using a Beckman Zeromatic pH meter.

RESULTS

The results of the variation of acid treatment on the pH of latex and the PRI of crepe coagulum are given in Table 1. A slight reduction in PRI was only noticed when the pH of coagulation was below 3. This happened only when three times the normal dosage of HCl was added as a 0.5% solution. Earlier workers have explained that this lowering of pH could result in an adsorption of HCl on the rubber causing a degradation of properties. IR spectroscopy did not reveal anything abnormal and there was no conclusive evidence to show that there was any adsorption or addition of HCl to the rubber molecule. Our experiments also show that when normal dosages are used there is no significant difference between the cure rate of HCl coagulated rubber and formic acid coagulated rubber. However, the cure rate of RSS is faster than the cure rate of crepe rubber irrespective of the nature of the coagulant additive (Table 2). This is due to the removal of first fraction rubber prior to coagulation.

TABLE 1

EFFECT OF COAGULANT ADDITIVE ON THE pH OF LATEX AND THE PRI OF CREPE RUBBER PREPARED FROM IT

Coagulant additive l per Kg of rubber		pH of latex after adding acid	PRI
0.5% HCl	0.3 ($\frac{1}{2}$×N)	5.0	81
	0.6 (N)	4.5	79
	0.9 (1$\frac{1}{2}$×N)	4.0	86
	1.2 (2 ×N)	3.5	78
	1.5 (2$\frac{1}{2}$×N)	2.5	60
1% HCOOH	0.3 (N)	5.0	87
	0.6 (2 ×N)	4.5	79
	0.9 (3 ×N)	4.0	78
	1.2 (4 ×N)	3.5	80
2% CH_3COOH	0.3 (N)	5.5	88
	0.6 (2 ×N)	4.0	84
	0.9 (3 ×N)	4.5	82
	1.2 (4 ×N)	4.0	83
	1.5 (5 ×N)	3.5	74

(N—Normal dosage)

TABLE 2

EFFECT OF COAGULANT ADDITIVE ON THE "CURE RATE"

Sample	Raw Mooney viscosity	ACS 1 COMPOUND		
		T.C. strain	Mooney scorch at 120°C	Compound viscosity
RA	99	66	10 min	62
RB	99	65	8 ,,	60
RC	92	64	11 ,,	58
CA	91	98	14 ,,	49
CB	93	101	15½ ,,	49
CC	95	94	14 ,,	51

RA—RSS coagulated with 0.6 l of 0.5% HCl/Kg of rubber

RB—RSS coagulated with 0.9 l of 0.5% HCl/Kg of rubber

RC—RSS coagulated with 0.3 l of 1.0% Formic Acid/Kg of rubber

CA—Crepe rubber coagulated with 0.6 l of 0.5% HCl/Kg of rubber

CB—Crepe rubber coagulated with 0.9 l of 0.5% HCl/Kg of rubber

CC—Crepe rubber coagulated with 0.3 l of 1.0% Formic Acid/Kg of rubber

Ageing properties of raw rubber

In order to evaluate the oxidisability of the raw rubber an exhaustive series of PRI tests were carried out on raw rubber prepared by HCl coagulation at 2 levels of concentration (Normal and 1½ times Normal).

PRI tests were done:

(a) Before ageing

(b) After accelerated ageing at 50 °C and 70 °C for periods ranging from 1 h to 1 week

(c) After accelerated ageing in the oxygen bomb under a pressure of 2.07 MN/m^2 for 30 min at 70 °C

(d) After shelf ageing for 1 year.

The results given in Table 3 indicate that the rubber produced by controlled coagulation with HCl is superior in resistance to ageing when compared with the rubber prepared using a standard coagulant like formic acid (Table 3).

TABLE 3

PRI OF RAW RUBBER AFTER ACCELERATED AGEING

Type of rubber	Coagulant additive	Coagulant concentration (l/kg rubber)	PRI before accelerated ageing	PRI after accelerated ageing in an oven												PRI after ageing in oxygen bomb for 30 min at 70 °C under a pressure of 2.07MN/m²	PRI after shelf ageing for 1yr
				50 °C						70 °C							
				1h	2h	3h	24h	48h	1wk	1h	2h	3h	24h	48h	1wk		
Pale crepe	0.5% hydrochloric acid	0.6	71	87	82	80	66	83	71	71	71	75	80	71	—	31	79
	0.5% hydrochloric acid	0.9	71	77	77	78	66	81	68	67	67	70	76	71	—	32	70
	1.0% formic acid	0.3	74	79	80	82	67	83	63	58	58	63	74	69	—	20	72
RSS	0.5% hydrochloric acid	0.6	77.4	82	79	81	82	81	80	80	81	78	82	73	59	73	73
	0.5% hydrochloric acid	0.9	80.6	80	75	76	66	80	82	75	75	77	78	74	53	58	72
	1.0% formic acid	0.3	81.7	78	76	75	76	74	72	70	74	75	56	45	35	53	75

Ageing of unprotected and protected gum vulcanisates

The ageing properties of unprotected and protected gum sulphur/CBS vulcanizates, (see Appendix I) with reference to lowering of tensile strength are given in Table 4. As expected, in keeping with the high PRI of the raw rubber, all the types tested showed good ageing properties in the presence or an antioxidant. In the absence of an antioxidant the aged tensile strength dropped drastically and here again the HCl coagulated rubber was more resistant to ageing than the formic acid coagulated rubber (see Table 4).

TABLE 4

TENSILE STRENGTH OF GUM VULCANIZATES (kg/cm^2)

Sample	With antioxidant		With out antioxidant	
	Unaged	Aged for 2 days at 100°C	Unaged	Aged for 2 days at 100°C
RA	221	178	215	81
RB	224	188	216	91
RC	229	162	223	43
CA	202	143	200	29
CC	220	177	216	16

(See Table 2 for sample descriptions)

CONCLUSION

Use of hydrochloric acid as a coagulant in the amounts used in our experiments, *i.e.* 0.6 to 0.9 l of 0.5% HCl per Kg of dry rubber has no deleterious effects on the properties of raw rubber, and all samples examined had better ageing properties than formic acid coagulated rubber. It would be seen that the use of excessive quantities of HCl during the coagulation of latex will cause some deterioration in the rubber. One reason in favour of the use of HCl is economy (see Appendix II) and it does not seem logical that the producer would use more acid than is necessary and thereby increase his coagulation costs. There is no objection to the use of HCl in carefully supervised dosages as an economic measure, and to conserve foreign exchange which is so vital to us and also as a substitute for formic acid when it runs short in the market.

Therefore, under carefully controlled conditions it can be a practicable proposition to use HCl as a coagulant for natural rubber latex.

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APPENDIX I

COMPOUNDING FORMULATION AND CURING CONDITIONS

Ingredients	Parts by weight	
	A	B
Rubber	100	100
Nonox HFN	1	—
Zinc Oxide	5	5
Stearic Acid	2	2
Sulphur	2.5	2.5
CBS	0.5	0.5
Vulcanizing temperature (°C)	140	
Cure time (min)	40	
A-Protected gum vulcanizate	—	—
B-Unprotected gum vulcanizate	—	—

Nonox HFN — Phenolic antioxidant
CBS — N-cyclohexyl2-benzothiazy-sulphenamide

APPENDIX II

Cost of Coagulant

A HCl

At the rate of 0.6 l HCl (0.5%) per kg of rubber :—
100 kg of rubber will require 0.857 l of commercial HCl (35%)
Cost of one ton of commercial HCl (35%) =Rs. 1,000/-

$$\text{Cost of 0.857 l of HCl (35\%)} = \frac{1{,}000 \times 0.857}{2{,}240 \times 4.5} \times 11.4$$

Cost of coagulation with HCl =Rs. 0.97 per 100 kg rubber

B Formic Acid

At the rate of 0.3 HCOOH (1%) per kg of rubber
100 kg of rubber will require 0.33 l of commercial HCOOH (90%)
Cost of one kg of commercial HCOOH (90%) = Rs. 3.71
Cost of 0.33 l of HCOOH (90%) = 3.71 x 0.33 x 1.202
Cost of coagulation with HCOOH = Rs. 1.46 per 100 kg rubber