

PATENT SPECIFICATION



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COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in the Inhibition of Volatile Acid Formation in Preserved Latex

We, THE NATURAL RUBBER PRODUCERS RESEARCH ASSOCIATION, formerly known as THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, a Body Corporate duly organised under the Laws of Great Britain, of 19, Fenchurch Street, London, E.C.3., do hereby declare the invention (which has been communicated to us by Kalyanaramaiyer Chandrasekaran and William George Wren, both British Subjects of The Rubber Research Institute of Malay, Kuala Lumpur, Malaya), for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the inhibition of volatile fatty acid formation in preserved latex during the long period which may elapse and which may amount to several weeks and months between the addition of the preservative and the subsequent treatment of the latex, as a raw material in the manufacture of rubber articles.

It has frequently been observed that powerful bactericides are not adequate in themselves to prevent slow deterioration of concentrates prepared from Hevea latex. Earlier work carried out by us demonstrated that the use of (a) a mild alkali, (b) a bactericide, and (c) a sequestering agent for divalent metal ions, gave many combinations which were effective as preservative systems, and formed the subject of Patent Specification No. 800,089. Further study has shown that whilst some bactericides are effective in latex and latex concentrates for killing bacteria and maintaining the latex in a liquid condition, they do not prevent long term spoilage of the latex, as evidenced by the development of volatile fatty acids (v.f.a.). Many instances have been examined where the viable bacteria count is low throughout

the storage period, but marked increase in v.f.a. has occurred. Concomitant with increased v.f.a. there is an increase in the KOH number, increase in electrical conductivity, decrease in mechanical stability, which render the latex less suitable for normal industrial application.

The origin of the v.f.a. in imperfectly preserved latices is not known. It appears to be independent of viable bacteria, and may be produced by enzymic or chemical processes. The following table demonstrates the effect of preservative systems applied to portions from the same bulk of latex concentrate, in some of which the count of viable bacteria is low, but v.f.a. development is considerable:

Preservative	% by Weight latex	Age of latex Days	V.F.A. No.*	Viable Bacteria per ml.
Ammonia (Control)	0.7	10	0.02	5
Ammonia (Control)	0.2	10	0.29	1.05×10^3
Ammonia Antibiotics	0.2)	10	0.24	6
Ammonia Sulphonamide derivatives.	0.2)	10	0.28	8.2

It is quite possible that dead bacterial cells may be the source of enzymes producing the change.

The present invention is concerned with a method of suppressing such volatile acid formation by the addition to the latex of a

* The determination of volatile fatty acids is described in the Journal of the Rubber Research Institute of Malaya Vol. 14 Communication No. 281.

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substance which is an enzyme poison.

Substances which have been found effective in inhibiting v.f.a. formation include salts of certain metals, such as copper, silver and nickel, which are well-known enzyme poisons. These substances are of interest in demonstrating the principle claimed in this application, viz. the inhibition of v.f.a. formation by certain enzyme poisons, but are not considered very suitable for commercial application, copper because of its well-known activity as a catalyst of oxidation for rubber, silver owing to high cost. Other well-known enzyme poisons such as sodium fluoride, semicarbazide hydrochloride, iodoacetic acid, have been found effective, but high concentrations have to be employed, which render their use costly, and undesirable in that other properties of the latex concentrates may be adversely affected.

An enzyme poison which has been found very effective and reasonably free from these defects in zinc oxide, which has been used at concentrations between 0.01 and 0.2 per cent on the latex concentrate (weight for weight).

The following examples demonstrate the principles involved in and the method of operating the process claimed. In the examples when antibiotics were employed they consisted of the following:—

	<i>p.p.m. (on latex).</i>
Streptomycin ...	40
Oxytetracycline ...	4
Chlortetracycline ...	1
Penicillin ...	1

For purposes of dispersion 0.02 per cent chlorinated trisodium phosphate together with 0.05 per cent detergent Polyrad P 2000 W were employed.

The antibiotic dispersion is prepared by weighing out the required amounts of antibiotics separately into sterile isotonic saline solution (0.85% NaCl) to give a 5% by weight slurry or dispersion. Polyrad P 2000 W is the compound formed when 1 mol of the amine, dehydro-abietyl amine is condensed with 20 mols. of ethylene oxide. It is used as a 10% by weight solution in distilled water.

The order of addition is as follows:—

Firstly 0.02% (on latex) of chlorinated trisodium phosphate.

Secondly 0.05% (on latex) of detergent Polyrad P 2000 W.

Lastly the antibiotics, with streptomycin first. In the example where sulphonamides were employed they consisted of the following:—

	<i>p.p.m. (on latex).</i>
Sulphanilamide ...	500
Sulphathiazolium ...	100
Sulphaguanidine ...	50
Phthalyl sulphathiazole ...	50
Sulphamerazine ...	50
Alternative combinations which have been	

tried with similar results are:—

	<i>p.p.m. (on latex).</i>
Sulphathiazolium ...	500
Sulphapyridine ...	50
Sulphaguanidine ...	50
Succinyl sulphathiazole ...	50
Phthalyl sulphathiazole ...	50

and

	<i>p.p.m. (on latex).</i>
Phthalyl sulphathiazole ...	500
Sulphathiazolium ...	100
Sulphapyridine ...	50
Sulphaguanidine ...	50
Sulphamerazine ...	50

The dispersions of sulphonamide derivatives are prepared as follows:—

Weigh the required quantities of sulphonamides separately into distilled water to make a 5% slurry in each case. Add a drop or two (as little as possible) of 2N.NaOH with shaking until a solution is obtained in each case. The Polyrad P 2000 W is made up as a 10% by weight solution in distilled water, and the ingredients are added in the following order:—

Firstly 0.5% (on latex) of the Polyrad P 2000 W, then the sulphonamides in the order given in the description, that is with the highest concentration sulphonamide leading.

Example 1.

The use of copper chloride for inhibiting v.f.a. formation in latex concentrates preserved with low ammonia content is demonstrated in Table 1.

The concentrate was prepared by centrifuging field latex containing 0.3 per cent ammonia (by weight). The ammonia content of the concentrate was adjusted to 0.2 per cent, and separate portions were treated with antibiotics, sulphonamide derivatives and cupric chloride, as set out in Table 1. The development of v.f.a. in concentrates preserved with 0.2% ammonia, together with antibiotics and 0.2% ammonia together with sulphonamide derivatives, is clearly seen. In the presence of copper chloride, however, the formation of v.f.a. is markedly inhibited.

As is well-known, the use of copper in latex concentrates is not practicable, owing to the readiness with which copper compounds catalyse oxidation of the rubber hydrocarbon. The example is included to demonstrate the principle claimed, viz. the inhibition of v.f.a. formation by enzyme poisons.

Example 2.

Table 2 demonstrates the effectiveness of silver nitrate in preventing the development of v.f.a. in latex concentrates of low ammonia content. The bactericide and enzyme poison were added to the latex after centrifuging and adjusting the ammonia content to 0.2 per cent.



0.2% ammonia

It is doubtful whether silver nitrate can find commercial application in latex concentrates owing to its relatively high cost.

Example 3.

- 5 Nickel chloride has been found effective in preventing v.f.a. formation in certain instances. Table 3 demonstrates the application of nickel chloride.

Example 4.

- 10 A number of organic enzyme poisons have been investigated, one of the most effective being semicarbazide hydrochloride.

Inhibition of v.f.a. formation by this reagent is demonstrated in Table 4.

- 15 *Example 5.*

- One of the most effective methods of reducing v.f.a. formation in ammoniated latex concentrates has been found to consist in the addition of zinc oxide, as an aqueous suspension, subsequent to the centrifuging operation.

- This reagent is very effective with both high and low concentrations of ammonia, and has none of the objections shown by the previous examples.

- It should be recorded, however, that latices matured in the presence of zinc oxide fail to develop mechanical stabilities high enough for industrial use. The addition of small amounts of a stabilising agent is therefore required to bring properties into line with industrial requirements. It is essential to use stabilisers which do not interfere with the subsequent use of the latex as a raw materials for the manufacture of rubber articles. Such materials are long chain fatty acids. In the present work, lauric acid has been largely employed, but others, such as oleic, linoleic, linolenic, myristic, are equally suitable. Other materials which are also effective comprise sulphonated detergents such as turkey red oil, sulphonated lorol.

- Of the substances tried for reducing v.f.a. formation in latex concentrates, it will be seen from the foregoing that zinc oxide is one of the most effective. Owing to its comparatively low cost and ease of handling it has been studied more extensively than the other possible reagent. Zinc oxide is commonly added to latex when compounded by consumers with a range of materials for the purpose of producing a vulcanized article. The amount added is usually between 1% and 5% by weight calculated on the rubber content of the latex. Such latex tends to thicken on storage and cannot be kept for long periods. In our process the zinc oxide is added to the latex within a day or two of obtaining it from the tree, at a time when months and years may elapse before it is compounded for use in the manufacture of rubber articles. The amount of zinc oxide which is added does not exceed 0.2% which is insufficient to cause thickening in association with the other preservative specified

even though the latex is stored for very long periods before it is compounded and processed in the usual way for the manufacture of rubber articles. Many combinations of bactericide with zinc oxide are set out in Table 5, which clearly demonstrates the marked inhibition of v.f.a. formation on introducing zinc oxide. Without the addition of zinc oxide the combination of low ammonia and bactericide is generally ineffective and concentrates so prepared are liable to the chemical changes which produce volatile fatty acids in latex concentrate during the period which elapses between its preparation and eventual use as a raw material in the manufacture of rubber articles.

Example 6.

An alternative method of utilising zinc oxide has been worked out, in which field latex is ammoniated to 0.3 per cent, and zinc oxide is added as suspension before centrifuging. The latex is then allowed to stand, preferably overnight, before commencing the centrifuging operation, which removes most of the insoluble zinc compounds present. The ammonia content of the concentrate is then adjusted to the required amount and the desired bactericide added.

The data given in Table 6 demonstrates the inhibition of v.f.a. formation obtained.

To demonstrate the application of the principle herein claimed to the preparation of latex concentrates suitable for industrial use, the following examples are given:—

Example 7.

Field latex containing 0.3 per cent ammonia (by weight) was centrifuged in the usual manner to give a concentrate of approximately 60 per cent dry rubber content, containing about 0.15 per cent ammonia. The ammonia content was then adjusted to 0.2 per cent and the following materials added:—

	Per cent (by weight)
Lauric acid* ...	0.03
Mercaptobenzthiazole ...	0.05
Zinc oxide φ ...	0.05
* Added as 20% solution of ammonium laurate.	
φ Added as dispersion comprising:—	
Zinc oxide ...	50
Gum acacia ...	0.4
Potassium hydroxide ...	0.2
Water ...	49.4

The mercaptobenzthiazole is added to the latex as a 50% dispersion after ball-milling for 24 hours, the dispersion being made up as follows:—

Mercaptobenzthiazole — 100 parts
Dispersol* LR (Disodium methylene dinaphthalene sulphonate) 5% solution in water — 100 parts.

* Registered Trade Mark.



The concentrate thus prepared remained sweet and in good condition throughout the period of observation, i.e. for about six months.

5 Mechanical stability (A.S.T.M.) results were as follows:—

	Days after preparation.	Mechanical stability (seconds)
	10	150
10	30	780
	90	725

A similar preparation containing 0.10 per cent mercaptobenzthiazole showed the following data:

	Days after preparation.	Mechanical stability (seconds)
15	10	100
	30	655
	90	655

20 Example 8.

Field latex was concentrated in the usual way, and the ammonia content adjusted to 0.2 per cent followed by the addition of lauric acid, cyclohexyl benzthiazyl sulphenamide and zinc oxide.

25 The concentrates produced remained sweet and in good condition throughout the period of observation i.e. for about six months.

30 Mechanical stability data are as follows:—

Composition			
Lauric Acid	Cyclohexyl-benzthiazyl sulphenamide	Zinc Oxide	Mechanical stability (A.S.T.M.)* after 30 days (Seconds)
0.05	0.05	0.05	690
0.05	0.05	0.10	565

40 * The mechanical stability is determined by the method of the American Society for Testing Materials, A.S.T.M. D1076-54T.

Example 9.

A concentrate was prepared in the usual way, the additives being as follows:—

	Per cent (by weight)
Ammonia	0.2
Sodium pentachlorophenate	0.1
Lauric acid	0.05
Zinc oxide	0.05

The concentrate thus prepared was sweet 50 and has remained in good condition for over six months.

Mechanical stability results are as follows:—

Days after preparation.	Mechanical stability (A.S.T.M.) Seconds.
10	1310
30	1530
90	1445

Example 10.

The addition of zinc oxide to the preservative system described in our co-pending application No. 38683/56 (Serial No. 821,872) in which selenium dimethyl dithiocarbamate is used to preserve latex in the presence of a little ammonia enables the amount of selenium dimethyl dithiocarbamate necessary for full preservation to be reduced from 0.04% to below 0.01%.

Field latex was treated with 0.3% ammonia and centrifuged according to standard practice. The centrifuged latex was ammoniated to 0.2% ammonia by weight and treated with 0.01 to 0.03% selenium dimethyl dithiocarbamate, 0.05% lauric acid as ammonium laurate, and 0.02 to 0.05% zinc oxide.

The latex was fully preserved after one and three months storage and showed satisfactory V.F.A. Number and development of mechanical stability. The results are shown in Table 7. In this table, results are also given for the same latex centrifuged and preserved by conventional means with 0.7% ammonia alone.

Table 1

Effect of Cupric Chloride on V.F.A. No.

Bactericidal System		Age of latex. Days.	V.F.A. ~~Now~~ in presence of following amounts cupric chloride per cent on latex.				
			Nil	0.01	0.05	0.10	
90	Ammonia	0.2	10	0.26	0.04	0.03	0.03
				Coagulated	0.14	0.03	0.03
	Ammonia	0.2	10	0.23	0.03	0.02	0.03
	Antibiotics		30	0.35	0.04	0.03	0.03
95	Ammonia	0.2)	10	0.30	0.06	0.03	0.03
	Sulphonamide derivatives	)	30	0.37	0.10	0.03	0.03



Table 2
Effect of Silver Nitrate on V.F.A. No.

5	Bactericidal System		Age of latex. Days.	V.F.A. No. in presence of following amounts silver nitrate per cent on latex.			
				Nil	0.01	0.05	0.10
10	Ammonia	0.2	10	0.26	0.14	0.02	0.02
			30	Coagulated	~~0.02~~	0.11	0.02
	Ammonia	0.2)	10	0.23	0.02	0.03	0.02
	Antibiotics	)	30	0.35	0.02	0.03	0.02
	Ammonia	0.2)	10	0.30	0.06	0.03	0.02
	Sulphonamide derivatives	)	30	0.37	0.12	0.03	0.05
	Ammonia	0.2)	10	0.26	—	—	0.02
	Sodium Penta chlorphenate	)	30	Pasty	—	—	0.02
		0.10)	90	—	—	—	0.03

Table 3
Effect of Nickel Chloride

20	Bactericidal System		Age of latex. Days.	V.F.A. No. in presence of following amounts nickel chloride per cent on latex.		
				Nil	0.05	0.10
25	Ammonia	0.2)	10	Coagulated	0.14	0.02
	Mercaptobenz-thiazole	0.05)	30	Coagulated	0.37	0.03

Table 4
Effect of Semicarbazide hydrochloride

30	Bactericidal System		Age of latex. Days.	V.F.A. No. in presence of following amounts Semicarbazide hydrochloride per cent on latex.	
				Nil	0.15
	Ammonia	0.03)	10	0.19	0.02
	Antibiotics	)	30	0.22	0.16



/ 0.20

Table 5
Effect of Zinc Oxide

	Bactericidal System		Age of latex. Days.	V.F.A. No. in presence of following amounts zinc oxide per cent on latex.		
5				Nil	0.05	0.1
	Ammonia	0.2	10	0.26	0.04	0.03
			30	Coagulated	0.13	0.03
10	Ammonia	0.2)	10	0.23	0.02	0.02
	Antibiotics	)	30	0.35	0.02	0.02
	Ammonia	0.2)	10	0.30	0.02	0.02
	Sulphonamide derivatives	)	30	0.37	0.02	0.02
	Ammonia	0.2)	10	0.49	0.02	0.03
15	Dichlor-m-xyleneol	0.10)	30	0.65	0.04	0.04
	Ammonia	0.2)	10	0.46	0.03	0.03
	6-Chloro o-cresol	0.1)	30	0.56	0.04	0.04
	Ammonia	0.2)	10	0.26	0.01	0.02
20	Sodium penta-chlorophenate	0.1)	30	Pasty	0.01	0.02
			90	Coagulated	0.03	0.03
	Ammonia	0.2)	10	Coagulated	0.36	0.02
	Boric acid	0.05)	30	Coagulated	Coagulated	0.03
	Ammonia	0.2)	10	Coagulated		—
25	Mercaptobenzthiazole	0.05)	30	Coagulated	0.03	—
			90	Coagulated	0.02	—
	Ammonia	0.2)	10	0.26	0.02	—
	Mercaptobenzthiazole	0.10)	30	0.30	0.02	—
			90	0.40	0.02	—
30	Ammonia	0.2)	10	0.17	0.03	0.03
	Piperidine	)	30	0.36	0.03	0.04
	pontamethylene dithiocarbamate	)	90	Coagulated	0.02	0.02
	Ammonia	0.2)	10	0.36	0.03	0.03
35	Aniline	)	30	Coagulated	0.03	0.03
	formaldehyde condensate [AlO]	)	90	Coagulated	0.03	0.02
	Ammonia	0.2)	10	0.41	0.03	0.02
	Cyclohexyl benzthiazyl	)	30	0.55	0.04	0.03
40	sulphenamide	)	90	Coagulated	0.05	0.02
		0.10)				
	Ammonia	0.2)	10	0.11	0.02	—
	Diphenyl guanidine	)	30	0.34	0.02	—
		0.10)	90	0.42	0.02	—
	Ammonia	0.2)	10	0.38	0.03	0.03
45	Hexamethylene tetramine	)	30	Coagulated	0.05	0.03
		0.10)				



penta

Table 6
Effect of Zinc Oxide, added before centrifuging.

5	Bactericidal System	Age of latex. Days.	V.F.A. No.	
			No zinc oxide added.	0.05 per cent zinc oxide added to field latex before centrifuging.
10	Ammonia 0.2	10	0.03	0.05
	Ammonia 0.2)	10	0.24	0.02
	Mercaptobenz-thiazole 0.05)			
15	Ammonia 0.2)	10	0.26	0.06
	Dichlor m-xyleneol 0.10)	10	0.28	0.04
	Ammonia 0.2)			
	6-Chloro o-cresol 0.10)			

Table 7
Effect of zinc oxide on latex concentrate preserved with low concentrations of ammonia and selenium dimethyl dithiocarbamate.



	% Zinc oxide on Latex.	% Selenium compound on Latex.	% Ammonia on Latex.	% Lauric as ammonium soap on Latex.	Age in days.	V.F.A. No.	Mechanical Stability (Secs)
25	Nil	Nil	0.70	Nil	10	0.01	210
					30	0.01	985
					90	0.02	1120
	Nil	0.03	0.20	0.05	10	0.01	80
					30	0.18	860
					90	0.32	135
30	0.02	0.03	0.20	0.05	10	0.01	85
					30	0.01	1170
					90	0.02	1685
	0.05	0.03	0.20	0.05	10	0.01	100
					30	0.01	850
					90	0.02	1050
35	0.02	0.01	0.20	0.05	10	0.01	90
					30	0.01	1430
					90	0.02	1925
40	0.05	0.01	0.20	0.05	10	0.01	100
					30	0.01	980
					90	0.02	1200

WHAT WE CLAIM IS:—

1. A process for inhibiting volatile fatty acid formation in preserved, concentrated latex from *Hevea brasiliensis* during the period which elapses between preservation and the eventual use of the latex as a raw

material in the manufacture of rubber articles, including the step of adding to the latex before or immediately after concentration, a small proportion of a substance which is an enzyme poison as herein defined.

Table 6
Effect of Zinc Oxide, added before centrifuging.

Bactericidal System	Age of latex. Days.	V.F.A. No.	
		No zinc oxide added.	0.05 per cent zinc oxide added to field latex before centrifuging.
10 Ammonia 0.2)	10	0.03	0.05
Ammonia 0.2)	10	0.24	0.02
Mercaptobenz-thiazole 0.05)			
Ammonia 0.2)	10	0.26	0.06
15 Dichlor m-xyleneol 0.10)	10	0.28	0.04
Ammonia 0.2)	10	0.28	0.04
6-Chloro o-cresol 0.10)			

Table 7.

Effect of zinc oxide on latex concentrate preserved with low concentrations of ammonia and selenium dimethyl dithiocarbamate.

	% Zinc oxide on Latex.	% Selenium compound on Latex.	% Ammonia on Latex.	% Lauric as ammonium soap on Latex.	Age in days.	V.F.A. No.	Mechanical Stability (Secs)
25	Nil	Nil	0.70	Nil	10	0.01	210
					30	0.01	985
					90	0.02	1120
30	Nil	0.03	0.20	0.05	10	0.01	80
					30	0.18	860
					90	0.32	135
35	0.02	0.03	0.20	0.05	10	0.01	85
					30	0.01	1170
					90	0.02	1685
40	0.05	0.03	0.20	0.05	10	0.01	100
					30	0.01	850
					90	0.02	1050
45	0.02	0.01	0.20	0.05	10	0.01	90
					30	0.01	1430
					90	0.02	1925
50	0.05	0.01	0.20	0.05	10	0.01	100
					30	0.01	980
					90	0.02	1200

WHAT WE CLAIM IS:—

1. A process for inhibiting volatile fatty acid formation in preserved, concentrated latex from *Hevea brasiliensis* during the period which elapses between preservation and the eventual use of the latex as a raw

material in the manufacture of rubber articles, including the step of adding to the latex before or immediately after concentration, a small proportion of a substance which is an enzyme poison as herein defined.





Sulphathiazole

2. A process for the inhibition of reactions which form volatile fatty acids in preserved rubber latex from *Hevea Brasiliensis*, including the step of adding up to 5 0.2% zinc oxide to the preserved latex before or immediately after concentration.

3. A process according to either of the preceding claims wherein zinc oxide is added as an aqueous suspension before 10 centrifuging in order that any insoluble zinc compounds are removed by settling out and by subsequent centrifuging.

4. A process according to any of the preceding claims wherein the mechanical stability of the preserved latex is enhanced by 15 the presence of a small amount of a long chain fatty acid as stabilising agent.

5. A process according to any of the preceding claims comprising the steps of ammoniating field latex to 0.3% adding zinc 20 oxide as an aqueous suspension, allowing the latex to stand, and centrifuging to the desired concentration of approximately 60% dry rubber content.

6. A process according to the preceding Claim 5 wherein, when the latex has been centrifuged to give a concentration of approximately 60% dry rubber content, the ammonia content is adjusted to 0.2% and 30 wherein there are then added a small proportion of the order of 0.05% by weight of the zinc oxide, a long chain fatty acid and bactericide.

7. A process according to claim 6 wherein a small proportion of the order of 0.001% to 0.01% of one or more antibiotics is present as bactericide.

8. A process according to either of the preceding claims 6 or 7 wherein there is 40 present 0.02%-0.2% of one or more sul-

phonamides such as sulphanilamide, sulphathiazolium, sulphaguanidine, phthalyl sulphathiazole or sulphamerazine as bactericide.

9. A process according to any of the preceding claims 6-8 wherein there is present about 0.1% of one or more chlorinated phenols or xylenols or their sodium salts such as 6-chloro o-cresol, pentachlorophenol or dichlor m-xenol as bactericide. 45

10. A process according to any of the preceding claims 6-9 wherein there is present as bactericide about 0.05% of boric acid or its ammonium salt. 50

11. A process according to any of the preceding claims wherein there is present a bactericide which is an accelerator of vulcanization such a mercaptobenzthiozole, piperidine pentamethylene dithiocarbamate, aniline formaldehyde condensate, cyclohexyl benzthiazyl sulphenamid, diphenyl 55 guanidine, hexamethylene tetramine or selenium dimethyl dithiocarbamate in the proportions from 0.01 to 0.2%.

12. Rubber latex concentrates when preserved by the process according to any of the preceding claims. 60

13. Rubber latex concentrates when preserved and stabilised substantially as described. 65

14. A process for the inhibition of reactions which form volatile fatty acids in preserved concentrated latex from *Hevea Brasiliensis*, substantially as described. 70

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Agents for Applicants.

PROVISIONAL SPECIFICATION

Improvements in the Inhibition of Volatile Acid Formation in Preserved Latex

75 We, THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, a Body Corporate duly organised under the Laws of Great Britain, of 19, Fenchurch Street, London, E.C.3., do hereby declare this invention to be 80 described in the following statement which invention has been communicated to us by Kalyawaramaiyer Chandra Sekarau and William George Wren, both British Subjects, of the Rubber Research Institute of Malaya, 85 Kuala Lumpur, Malaya:—

This invention relates to the Inhibition of Volatile Fatty Acid formation in preserved latices.

It has frequently been observed that 90 powerful bactericides are not adequate in themselves to prevent deterioration of concentrates prepared from *Hevea* latex. Earlier work carried out by us demonstrated that the use of (a) a mild alkali, (b) a bac- 95 tericide, and (c) a sequestering agent for

divalent metal ions, gave many combinations which were effective as preservative systems. Further study has thrown more light on this problem and it has now been demonstrated that whilst some bactericides are effective in latex and latex concentrates for killing bacteria, they do not prevent spoilage of the latex, as evidenced by the development of volatile fatty acids, (v.f.a.). Many instances have been examined where the viable bacteria count is low throughout the storage period, but marked increase in v.f.a. has occurred. Concomitant with increased v.f.a. there is an increase in the KOH Number, increase in electrical conductivity, decrease 110 in mechanical stability, etc., which render the latex less suitable for normal industrial application.

The origin of the v.f.a. in imperfectly preserved latices is not known. It appears to be independent of viable bacteria, and may 115



* C L M S *



be produced by enzymic or chemical processes. The following data demonstrate the effect of preservative systems applied to portions from the same bulk of latex concentrates, in which the count of viable bacteria is low, but v.f.a. development is considerable:

for line 12
read line 14
and vice versa

Preservative	% by Weight on latex	Age of latex Days	V.F.A. No.*	Viable Bacteria per ml.
10 Ammonia (Control)	0.2	10	0.29	1.05×10^3
15 Ammonia (Control)	0.7	10	0.02	5
Ammonia Antibiotics	0.2)	10	0.24	6
Ammonia Sulphonamide derivatives.	0.2)	10	0.28	8.2

It is quite possible that dead bacterial cells may be the source of enzymes producing the change.

It has been observed, however, that development of v.f.a. in imperfectly preserved latices can be inhibited by certain agents. The present invention deals with substances and means of incorporating them in latex, which markedly reduce v.f.a. development and permit the latex to mature after preparation to a product suitable for use by the consuming industry.

Substances which have been found effective in inhibiting v.f.a. formation include salts of certain metals, such as copper, silver and nickel, which are well-known enzyme poisoners. These substances are of interest in demonstrating the principle claimed in this application, viz. the inhibition of v.f.a. formation by certain enzyme poisons, but are not considered very suitable for commercial application, copper because of its well-known activity as a catalyst of oxidation for rubber, silver owing to high cost. Other well-known enzyme poisoners such as sodium fluoride, semicarbazide hydrochloride, iodoacetic acid, etc. have been found effective, but high concentrations have to be employed, which render their use costly and undesirable, in that other properties of the latex concentrates may be adversely affected.

A substance which has been found very effective and reasonably free from these defects is zinc oxide, which has been used at concentrations between 0.01 and 0.2 per cent on the latex concentrate (weight for weight).

The following examples demonstrate the principles involved in and the method of operating the process claimed.

Example 1.
The use of copper chloride for inhibiting v.f.a. formation in latex concentrates preserved with low ammonia content is demonstrated in Table 1.

Concentrate was prepared by centrifuging field latex containing 0.03 per cent ammonia, (by weight). The ammonia content of the concentrate was adjusted to 0.2 per cent, and separate portions treated with antibiotics, sulphonamide derivatives and cupric chloride, as set out in Table 1. The development of v.f.a. in concentrates preserved with 0.2% ammonia, 0.2% ammonia together with antibiotics and 0.2% ammonia together with sulphonamide derivatives, is clearly seen. In the presence of copper chloride, however, the formation of v.f.a. is markedly inhibited.

As is well-known the use of copper in latex concentrates is not practicable, owing to the readiness with which copper compounds catalyse oxidation of the rubber hydrocarbon. The example is included to demonstrate the principle claimed, viz., the inhibition of v.f.a. formation by enzyme poisoners.

In this and following examples the antibiotics employed comprised the following:—

	p.p.m. (on latex).	
Streptomycin	40	90
Terramycin	4	
Aureomycin	1	
Penicillin	1	

Other combinations have been tried and found effective, such as:

	p.p.m. (on latex).	
Streptomycin	100	
Terramycin	10	
Aureomycin	3	
Penicillin	3	100

For purposes of dispersion 0.02 per cent chlorinated trisodium phosphate together with 0.05 per cent detergent Polyrad P 2000W were employed.

For the present example and subsequent ones, the combination of sulphonamide derivatives employed was as follows:

	p.p.m. (on latex).	
Sulphanilamide	500	
Sulphathiazolium	100	110
Sulphaguanidine	50	
Phthalyl sulphathiazole	50	
Sulphamerazine	50	

Other combinations which have been found effective are:

	p.p.m. (on latex).	
Sulphathiazolium	500	
Sulphapyridine	50	
Sulphaguanidine	50	
Succinyl sulphathiazole	50	120
Phthalyl sulphathiazole	50	

and

	p.p.m. (on latex).	
Phthalyl sulphathiazole	500	
Sulphathiazolium	100	125
Sulphapyridine	50	
Sulphaguanidine	50	
Sulphamerazine	50	

For dispersion of the sulphonamide derivatives 0.05 per cent Polyrad P 2000W was employed.

Sulphamerazine



Example 2.

In Table 2 data are shown demonstrating the effectiveness of silver nitrate in preventing the development of v.f.a. in latex concentrates of low ammonia content. The bactericide and enzyme poisoner were added to the latex after centrifuging and adjusting the ammonia content to 0.2 per cent.

It is doubtful whether silver nitrate can find commercial application in latex concentrates owing to its relatively high cost.

Example 3.

Nickel chloride has been found effective in preventing v.f.a. formation in certain instances. It does not appear to be so generally applicable as copper and silver. Data demonstrating the application of nickel are given in Table 3.

Example 4.

A number of organic enzyme poisoners have been investigated, one of the most effective being semicarbazide hydrochloride.

Inhibition of v.f.a. formation by this reagent is demonstrated in Table 4.

Example 5.

One of the most effective methods of reducing v.f.a. formation in ammoniated latex concentrates has been found to consist in the addition of zinc oxide, as an aqueous suspension, subsequent to the centrifuging operation.

This reagent is very effective with both high and low concentrations of ammonia, and has none of the objections shown by the previous examples.

It should be recorded, however, that latices matured in the presence of zinc oxide fail to develop mechanical stabilities high enough for industrial use. The addition of small amounts of a stabilising agent is therefore required to bring properties into line with industrial requirements. It is essential to use stabilisers which do not interfere with subsequent coagulation processes to which the latex may be submitted. Such materials are long chain fatty acids, which occur naturally in latex. In the present work, lauric acid has been largely employed, but others, such as oleic, linoleic, linolenic, myristic, etc. are equally suitable. Other materials which are also effective comprise sulphonated detergents such as turkey red oil, sulphonated lorol, etc.

Of the substances tried for reducing v.f.a. formation in latex concentrates, it will be seen from the foregoing that zinc oxide is one of the most effective. Owing to its comparatively low cost and ease of handling it has been studied more extensively than the other possible reagents. Many combinations of bactericide with zinc oxide are set out in Table 5, which clearly demonstrates the marked inhibition of v.f.a. formation on introducing zinc oxide. Without the addition of zinc oxide the combination of low ammonia and bactericide is generally ineffective and concentrates so prepared are liable

to the putrefactive changes which produce volatile fatty acids in the commercial production of latex concentrate.

Example 6.

An alternative method of utilising zinc oxide has been worked out, in which field latex is ammoniated to 0.3 per cent, and zinc oxide is added as suspension before centrifuging. The latex is then allowed to stand, preferably overnight, before commencing the centrifuging operation, which removes most of the insoluble zinc compounds present. The ammonia content of the concentrate is then adjusted to the required amount and the desired bactericide added.

The data given in Table 6 demonstrate the inhibition of v.f.a. formation obtained.

To demonstrate the application of the principle herein claimed to the preparation of latex concentrates suitable for industrial use, the following examples are given:—

Example 7.

Field latex containing 0.3 per cent ammonia (by weight) was centrifuged in the usual manner to give a concentrate of approximately 60 per cent dry rubber content, containing about 0.15 per cent ammonia. The ammonia content was then adjusted to 0.2 per cent and the following materials added:

Per cent (by weight)

Lauric acid*	0.03
Mercaptobenzthiazole	0.05
Zinc oxide	0.05
* Added as 20% solution of ammonium laurate.	
? Added as dispersion comprising:—	
Zinc oxide	50
Gum acacia	0.4
Potassium hydroxide	0.2
Water	49.4

The concentrate thus prepared remained sweet and in good condition throughout the period of observation to date (about six months).

Mechanical stability (A.S.T.M.) results were as follows:—

Days after preparation.	Mechanical stability (seconds)
10	150
30	780
90	725

A similar preparation containing 0.10 per cent mercaptobenzthiazole showed the following data:

Days after preparation.	Mechanical stability (seconds)
10	100
30	655
90	655

Example 8.

Field latex was concentrated in the usual way, and ammonia content adjusted to 0.2 per cent followed by the addition of lauric acid, cyclohexyl benzthiazyl sulphenamide and zinc oxide.

70

75

80

85

90

95

100

105

110

115

120

125

130

135



The concentrates produced remained sweet and in good condition throughout the period of observation to date (about six months).

Mechanical stability data are as follows:

Lauric Acid	Cyclohexyl benzthiazyl sulphenamide	Zinc Oxide	Mechanical Stability (A.S.T.M.) after 30 days (Seconds)
0.05	0.05	0.05	690
0.05	0.05	0.10	565

Example 9.

Concentrate was prepared in the usual way, the additives being as follows:—

	Per cent (by weight)
Ammonia	0.2
Sodium pentachlorophenate	0.1
Lauric acid	0.05
Zinc oxide	0.05

The concentrate thus prepared was sweet and has remained in good condition for over six months.

Mechanical stability results are as follows:—

Days after preparation.	Mechanical stability (A.S.T.M.) Seconds.
10	1310
30	1530
90	1445

Table 1

Effect of Cupric Chloride on V.F.A. No.

35	Bactericidal and Stabilising System	Age of latex. Days.	V.F.A. Now in presence of following amounts cupric chloride per cent on latex.				
			Nil	0.01	0.05	0.10	
40	Ammonia	0.2	10	0.26	0.04	0.03	0.03
	Ammonia	0.2	10	Coagulated	0.14	0.03	0.03
	Antibiotics		30	0.23	0.03	0.02	0.03
	Ammonia	0.2)	10	0.35	0.04	0.03	0.03
	Sulphonamide	)	30	0.30	0.06	0.03	0.03
	derivatives		30	0.37	0.10	0.03	0.03

Table 2

Effect of Silver Nitrate on V.F.A. No.

Bactericidal and Stabilising System			Age of latex. Days.	V.F.A. No. in presence of following amounts silver nitrate per cent on latex.			
				Nil	0.01	0.05	0.10
50	Ammonia	0.2	10	0.26	0.14	0.02	0.02
			30	Coagulated	~~0.02~~	0.11	0.02
	Ammonia	0.2)	10		0.23	0.02	0.03
	Antibiotics	)	30	0.35	0.02	0.03	0.02
55	Ammonia	0.2)	10	0.30	0.06	0.03	0.02
	Sulphonamide derivatives	)	30	0.37	0.12	0.03	0.05
		)					
	Ammonia	0.2)	10	0.26	—	—	0.02
	Sodium Penta chlorphenate	)	30	Pasty	—	—	0.02
		0.10)	90	—	—	—	0.03

Table 3

Effect of Nickel Chloride

Bactericidal and Stabilising System		Age of latex. Days.	V.F.A. No. in presence of following amounts nickel chloride per cent on latex.		
			Nil	0.05	0.10
Ammonia	0.2)	10	Coagulated	0.14	0.02
Mercaptobenz- thiazole	) 0.05)	30	Coagulated	0.37	0.03

Table 4
Effect of Semicarbazide hydrochloride

Bactericidal and Stabilising System	Age of latex. Days.	V.F.A. No. in presence of following amounts Semicarbazide hydrochloride per cent on latex.	
		Nil	0.15
Ammonia	10	0.19	0.02
Antibiotics	30	0.22	0.16

Table 5
Effect of Zinc Oxide

Bactericidal and Stabilising System	Age of latex. Days.	V.F.A. No. in presence of following amounts zinc oxide per cent on latex.		
		Nil	0.05	0.1
Ammonia	10	0.26	0.04	0.03
Ammonia	30	Coagulated	0.13	0.03
Ammonia	10	0.23	0.02	0.02
Antibiotics	30	0.35	0.02	0.02
Ammonia	10	0.30	0.02	0.02
Sulphonamide	30	0.37	0.02	0.02
derivatives				
Ammonia	10	0.49	0.02	0.03
Dichlor-m-xyleneol	30	0.65	0.04	0.04
Ammonia	10	0.46	0.03	0.03
6-Chloro o-cresol	30	0.56	0.04	0.04
Ammonia	10	0.26	0.01	0.02
Sodium penta-	30	Pasty	0.01	0.02
chlorphenate	90	Coagulated	0.03	0.03
Ammonia	10	Coagulated	0.36	0.02
Boric acid	30	Coagulated	Coagulated	0.03
Ammonia	10	Coagulated	0.02	—
Mercaptobenzthiazole	30	Coagulated	0.03	—
	90	Coagulated	0.02	—
Ammonia	10	0.26	0.02	—
Mercaptobenzthiazole	30	0.30	0.02	—
	90	0.40	0.02	—
Ammonia	10	0.17	0.03	0.03
Piperidine	30	0.36	0.03	0.04
pentamethylene	90	Coagulated	0.02	0.02
dithiocarbamate				
Ammonia	10	0.36	0.03	0.03
Aniline	30	Coagulated	0.03	0.03
formaldehyde	90	Coagulated	0.03	0.02
condensate [AlO]				
Ammonia	10	0.41	0.03	0.02
Cyclohexyl	30	0.55	0.04	0.03
benzthiazyl	90	Coagulated	0.05	0.02
sulphenamide				
Ammonia	10	0.11	0.02	—
Diphenyl	30	0.34	0.02	—
guanidine	90	0.42	0.02	—
Ammonia	10	0.38	0.03	0.03
Hexamethylene	30	Coagulated	0.05	0.03
tetramine.				

Table 6

Effect of Zinc Oxide, added before centrifuging.

	Bactericidal and Stabilising System	Age of latex. Days.	V.F.A. No.	
			No zinc oxide added.	0.05 per cent zinc oxide added to field latex before centrifuging.
5				
10	Ammonia 0.2	10	~~0.03~~	0.05
	Ammonia 0.2)			
	Mercaptobenz-)	10	0.24	0.02
	thiazole 0.05)			
	Ammonia 0.2)			
15	Dichlor m-xyleneol 0.10)	10	0.26	0.06
	Ammonia 0.2)			
	6-Chloro o-cresol 0.10)	10	0.28	0.04



0.30

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