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COMPLETE SPECIFICATION

Improvements in or relating to the Preservation of Rubber Latex

(A communication from WILLIAM GEORGE WREN, a British Subject, of the Rubber Research Institute of Malaya, of Kuala Lumpur, Malaya).

5 We, THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, (formerly known as The British Rubber Producers' Research Association), a British Body Corporate, of, 19 Fenchurch Street, London, E.C.3, do hereby
10 declare the invention, 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:—

15 This invention is for improvements in or relating to the preservation of rubber latex either in the form of field latex or in the form of a concentrated latex.

20 In order to ship latex from *Hevea brasiliensis* overseas to consuming countries, it is common practice to concentrate the latex collected from the tree, by centrifuging or creaming procedures and to preserve it against bacterial, enzymic and chemical degradation by the addition
25 of preservatives; the addition of preservatives is often carried out both before and after the concentration process.

30 For some years, the most popular and commonly-used preservative has been ammonia, which is commonly added to the latex in amounts ranging from 0.6 to 0.8 per cent by weight on the finished liquid concentrate.

35 The presence of such large amounts of ammonia in the product renders it offensive when used industrially and is often undesirable from a technical point of view. In many instances, steps are taken to reduce the level of ammonia in consuming factories to some 0.1 to 0.3 per cent and it would obviously be
40 an advantage to be able to market latex concentrate containing ammonia at this level. Unfortunately, such reduced amounts of ammonia are inadequate to preserve natural rubber latex

[Price 4s. 6d.]

from bacterial attack and rapid putrefaction occurs in latices preserved with only such
45 amounts of ammonia.

The use of secondary preservatives in conjunction with low levels of ammonia is already established and we have previously proposed the use of various secondary preservatives
50 one of which was boric acid and another of which was zinc oxide, both used in conjunction with reduced amounts of ammonia.

55 We have previously shown that 8-hydroxyquinoline behaves as a powerful bactericide when added to latex and is of considerable value in preserving latex and latex concentrates; we have also previously shown that this material will preserve latex when added
60 together with ammonia but the amounts required have been such that the use of this material has not proved to be economic.

65 We have now discovered that a strongly synergistic effect is obtained when the 8-hydroxyquinoline is used in relatively very low concentration together with ammonia and boric acid or ammonia and zinc oxide.

70 According to the present invention, therefore, there is provided a process for the preservation of rubber latex which comprises adding to field latex, or a concentrate prepared
75 therefrom, from 0.05 to 0.002% of 8-hydroxyquinoline, from 0.1 to 0.3% of ammonia and from 0.5 to 0.1% of boric acid and/or 0.1 to 0.01% of zinc oxide by weight of the latex.

80 The preferred amount of ammonia added to the latex is 0.2% by weight of the latex; the preferred amounts of the 8-hydroxyquinoline are from 0.02 to 0.005%, of boric acid 0.2% and of zinc oxide 0.05 to 0.03%, all by weight
85 of the latex.

The invention is particularly applicable to the treatment of concentrated latex which may be produced by centrifuging with or without chemical creaming.

References in the specification to concentrated latex mean latex which has been con-



centrated to the extent normal in the rubber industry so that the rubber content of the latex is increased to a value of about 60% by weight.

- 5 The following examples serve to illustrate the manner in which the invention may be carried into effect. In the tables featuring in the examples, the property of Mechanical Stability Time (shown as M.S.T.) is defined and tested in accordance with the American Society for Testing Materials Specifications and Tests D.1076-54T, and contents of volatile fatty acids (shown as V.F.A.) and that of KOH No. are determined as described in the 10 Journal of the Rubber Research Institute of Malaya, Volume 14, Communications Nos. 281 and 297: The following experiment is described to illustrate the technique of examination used and to show the effect of 8-hydroxyquinoline without the use of the secondary preservative.

- 15 Latex concentrate was prepared from field latex collected at our Experiment Station, Sungei Buloh, Federation of Malaya; the ammonia content after centrifuging was adjusted to 0.2 per cent by weight based on the latex. The concentrate was then deliberately contaminated with bacteria by adding about 20

one part per hundred of another concentrate known to have a high count of viable bacteria. In this manner, it was ensured that a virulent population of bacteria was present so that the effectiveness of the added systems of bactericides could be assessed.

From the thus-contaminated latex two 35 batches were prepared, a control batch to which only 0.03 per cent lauric acid was added, and an experimental batch to which 0.03 per cent lauric acid and 0.2 per cent 8-hydroxyquinoline were added. The lauric acid was added as a 20 per cent solution in water prepared by suspending the lauric acid in water and adding ammonia solution drop by drop until a clear solution is obtained: the acid improves the mechanical stability of the latex. 40 Too much ammonia causes thickening and is better avoided. The 8-hydroxyquinoline was added as a solution in water.

Samples of the latices were stored in closed full bottles; bacterial and technological tests were carried out at intervals up to three months after preparation. The results are shown in Table 1 and clearly demonstrate the marked bactericidal effect of 8-hydroxyquinoline. The technological behaviour of the latex preserved with the reagent is shown to be excellent. 55

TABLE 1

Additives (parts per 100 latex)	Properties after lapse of time	KOH No.	VFA	MST	Viable bacteria per ml.
(1) Ammonia 0.2 and Lauric Acid 0.03	1 week	0.83	0.36	100	2×10^8
	1 month	0.89	0.42	115	4×10^6
	3 months	1.10	0.46	110	6×10^6
(2) As (1), with 8-hydroxyquinoline 0.2	1 week	0.57	0.02	890	less than 10
	1 month	0.67	0.01	1330	sterile
	3 months	0.70	0.02	1310	sterile

EXAMPLE 1

- 60 A latex concentrate was prepared by centrifuging field latex in the usual manner, the final concentration of ammonia being adjusted to 0.2 parts per cent. The concentrate was then deliberately contaminated with bacteria in the manner described in the experiment above.

- 65 Portions of the contaminated latex were then treated with additional preservatives and bactericides as follows: To the first were added 0.03 per cent lauric acid and 0.2 per cent boric acid, to the second the same ingredients together with 0.02 per cent 8-hydroxyquinoline and to the third, the same ingredients with only 0.005 per cent 8-hydroxyquinoline.

- 70 Boric acid was added as a 20 per cent solution in water, to which ammonia is added to give a pH value between 9 and 10. The other 75

ingredients were added as described in the preceding experiment.

Samples of the latices were stored in closed full bottles and examined at intervals. The results of technological tests are shown in Table 2 from which it will be seen that the addition of 8-hydroxyquinoline, even at the exceedingly low level of 0.005 per cent, had a marked effect upon the bacterial population which was reduced from a level of 1×10^8 viable cells per ml to almost zero, and maintained the latex virtually sterile over the three-month period. The marked improvement in the latex properties resulting from the reduced bacterial population is apparent from the table. After three months storage, the KOH No. was 0.83 as compared with 1.47 for the control (A good figure for boric acid latex, since the boric acid itself is titrated in the 95



bactericides



bactericidal

KOH No. test. Correcting for boric acid content the figures would be 0.63 and 1.27 respectively). The volatile fatty acids content had been maintained at 0.01 throughout the three-month period compared with 0.05 for the control. A substantial increase in mechanical stability time had also been achieved.

TABLE 2

Additives (parts per 100 latex)	Properties after lapse of time	KOH	VFA	MST	Viab bacteria per ml.
(1) Ammonia 0.2	1 week	0.73	0.01	475	1×10^5
Lauric acid 0.03	1 month	0.78	0.02	480	1×10^5
Boric acid 0.2	3 months	1.47	0.05	465	1×10^5
(2) As with (1), with 8-hydroxyquinoline 0.02	1 week	0.70	0.01	715	Nil
	1 month	0.78	0.01	735	Nil
	3 months	0.81	0.01	575	Nil
(3) As (1), with 8-hydroxyquinoline 0.005	1 week	0.67	0.01	675	Nil
	1 month	0.75	0.01	685	2
	3 months	0.83	0.01	570	2

EXAMPLE 2

10 A latex concentrate contaminated with bacteria was prepared as described in the preceding experiment. Three portions of the bulk were then preserved as follows: To the first 0.03 per cent lauric acid and 0.05 per cent zinc oxide were added, to the second, the same ingredients with the addition of 0.02 per cent 8-hydroxyquinoline and to the third the same ingredients, but adding only 0.005 per cent of 8-hydroxyquinoline.

20 Zinc oxide was added as a 50 per cent dispersion in water, prepared according to the following formula which shows the parts by weight:—

Zinc oxide	100
Gum acacia	4
Potassium hydroxide	0.2
Water	95.8

The remaining ingredients were added in the manner described in the preceding examples.

The results of tests carried out on the samples are recorded in Table 3. It will be seen that, again, at the very low level of 0.005 per cent 8-hydroxyquinoline had proved to be a most effective bactericide, reducing the bacterial count after three months storage from 7×10^5 cells per ml. to zero. The improvement in latex properties brought about by 0.005 per cent of 8-hydroxyquinoline is remarkable. The KOH No. was 0.58 as compared with 0.90 for the control, and the volatile fatty acids content was 0.01 as compared with 0.29 for the control. The mechanical stability time had been increased from 150 to 570 seconds.

TABLE 3

Additives (parts per 100 latex)	Properties after lapse of time	KOH	VFA	MST	Viab bacteria per ml.
(1) Ammonia 0.2	1 week	0.45	0.03	300	3×10^5
Lauric acid 0.03	1 month	0.64	0.22	190	5×10^5
Zinc oxide 0.05	3 months	0.90	0.29	150	7×10^5
(2) As (1), with 8-hydroxyquinoline 0.02	1 week	0.49	0.01	455	Nil
	1 month	0.50	0.01	600	less than 10
	3 months	0.59	0.01	590	Nil
(3) As (1), with 8-hydroxyquinoline 0.005	1 week	0.51	0.01	395	3
	1 month	0.50	0.01	520	less than 10
	3 months	0.58	0.01	570	Nil

EXAMPLE 3

In this experiment, the ingredients employed were the same as those in Example 2, but the zinc oxide addition was reduced from 0.05 to 0.03 per cent.

The results were even more striking than in the preceding examples, since the control latex had completely coagulated within three months,

whereas samples of the same latex to which only 0.005 per cent of 8-hydroxyquinoline had been added, were not only liquid, but showed excellent properties, the bacterial count being zero, the KOH No. 0.54, the volatile fatty acids content 0.01 and the mechanical stability 560.

TABLE 4

Additives (Parts per 100 latex)	Properties after lapse of time	KOH No.	VFA	MST	Viable bacteria per ml.
(1) Ammonia 0.2 Zinc oxide 0.03	1 week 1 month	0.87 0.82	0.18 0.34	95 Latex thickened	1×10^5 3×10^6
Lauric acid 0.03	3 months	Latex coagulated			
(2) As (1), with 8-hydroxyquinoline 0.005	1 week 1 month 3 months	0.40 0.44 0.54	0.01 0.01 0.01	90 430 560	9 4 Nil

It will be seen by comparing the results obtained in the Examples with the results obtained in the preceding experiment that there is a very strong synergistic effect arising out of the use of boric acid and zinc oxide in conjunction with the 8-hydroxyquinoline the extent of which is such that superior results are obtained with amounts of the latter compound which are less than one tenth of that shown in the experiment. Thus, by the invention, it is now economically possible to use 8-hydroxyquinoline in the stabilisation of latex by reducing the amount thereof which would in the absence of the boric acid and zinc oxide, be necessary to achieve a satisfactory preservation of latices against deterioration due to bacterial infection.

WHAT WE CLAIM IS:—

1. A process for the preservation of rubber latex which comprises adding to field latex, or a concentrate prepared therefrom, from 0.05 to 0.002% of 8-hydroxyquinoline, from 0.1 to 0.3% of ammonia and from 0.5 to 0.1% of boric acid and/or 0.1 to 0.01% of zinc oxide by weight of the latex.

2. A process according to claim 1 wherein the amount of ammonia employed is 0.2% by weight of the latex.

3. A process according to claims 1 or 2 wherein the amount of 8-hydroxyquinoline employed is from 0.02 to 0.005% by weight of the latex.

4. A process according to any of the preceding claims wherein the amount of boric acid is employed is 0.2% by weight of the latex.

5. A process according to any of the preceding claims wherein the amount of zinc oxide employed is from 0.03 to 0.05% by weight of the latex.

6. A process according to any of the preceding claims wherein the latex is a concentrate prepared by centrifuging of field latex with or without chemical creaming.

7. A process for the preservation of rubber latex substantially as described with reference to any of the foregoing Examples 1, 2 and 3.

8. Rubber latex containing by weight thereof from 0.05 to 0.002% of 8-hydroxyquinoline, 0.1 to 0.3% of ammonia and 0.5 to 0.01% of boric acid and/or zinc oxide.

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EXAMPLE 3

In this experiment, the ingredients employed were the same as those in Example 2, but the zinc oxide addition was reduced from 0.05 to 0.03 per cent.

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Zinc oxide 0.03	1 month	0.82	0.34	Latex	3×10^5
				thickened	
Lauric acid 0.03	3 months		Latex coagulated		
(2) As (1), with	1 week	0.40	0.01	90	9
8-hydroxyquinoline	1 month	0.44	0.01	430	4
0.005	3 months	0.54	0.01	560	Nil

It will be seen by comparing the results obtained in the Examples with the results obtained in the preceding experiment that there is a very strong synergistic effect arising out of the use of boric acid and zinc oxide in conjunction with the 8-hydroxyquinoline the extent of which is such that superior results are obtained with amounts of the latter compound which are less than one tenth of that shown in the experiment. Thus, by the invention, it is now economically possible to use 8-hydroxyquinoline in the stabilisation of latex by reducing the amount thereof which would in the absence of the boric acid and zinc oxide, be necessary to achieve a satisfactory preservation of latices against deterioration due to bacterial infection.

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2. A process according to claim 1 wherein the amount of ammonia employed is 0.2% by weight of the latex.

3. A process according to claims 1 or 2 wherein the amount of 8-hydroxyquinoline employed is from 0.02 to 0.005% by weight of the latex.

4. A process according to any of the preceding claims wherein the amount of boric acid is employed is 0.2% by weight of the latex.

5. A process according to any of the preceding claims wherein the amount of zinc oxide employed is from 0.03 to 0.05% by weight of the latex.

6. A process according to any of the preceding claims wherein the latex is a concentrate prepared by centrifuging of field latex with or without chemical creaming.

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