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556

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(54) IMPROVEMENTS IN OR RELATING TO RUBBER LATEX PRODUCTS

(71) We, THE RUBBER RESEARCH INSTITUTE OF MALAYA, a Body Corporate of Malaysia, of 3rd Mile Ampang Road, Kuala Lumpur, Malaya, do hereby 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:—

Our prior Patent Specification No. 965,757 relates to a method of stabilising natural rubber against undesirable hardening on storage by adding to natural rubber latex a compound such as hydroxylamine. The latex is then coagulated in the usual way, and the hydroxylamine reduces or prevents hardening of the dry rubber on storage, thus making it more easily mixed and compounded at a later date by the rubber manufacturing industry. The said Patent Specification does not teach the addition of hydroxylamine to latex and the subsequent manufacture of rubber latex articles, because mixing and compounding are at least partly effected while the rubber is still in the latex state, so that age hardening problems do not arise.

However, we have now surprisingly found that the manufacture of rubber latex products from rubber latex concentrates which have previously been treated with hydroxylamine does have certain advantages.

The present invention accordingly provides a process for the manufacture of rubber latex products as hereinafter defined characterised in that the rubber latex used in the manufacture has been treated by adding hydroxylamine or an acid addition salt thereof to the rubber latex concentrate. This process is preferably performed immediately after concentration and before the rubber latex has been allowed to stand for any substantial length of time. The process should be performed preferably by the grower at the plantation, rather

than by the consumer at the time of compounding in the factory.

By the term "rubber latex product" we mean a rubber manufactured product formed from latex such that the rubber is formed into the shape of the product not later than coagulation or gelling of the rubber latex.

The hydroxylamine may be added to the latex either neat or as a solution in an inert solvent. It may be used either free or in the form of the hydrochloride, sulphate, phosphate or other salt, preferably at a concentration of from 0.05% to 2% by weight on the dry rubber content of the latex. The latex is derived from *Hevea brasiliensis*. It may be concentrated by any accepted method, for example, single or multiple centrifugation, creaming, evaporation or electrodecantation, and may be preserved in any way according to normal practice.

One aspect of the present invention arises from our discovery that the addition of hydroxylamine or an acid addition salt thereof to the latex concentrate immediately after concentration in the estate factory produces a latex which, on vulcanization gives a rubber of modulus reduced by from 5% to 50% measured at optimum vulcanization. When such a latex is used to prepare articles by dipping, e.g., gloves, it gives a softer product. In gloves, it gives a more sensitive "feel" to the user, more flexibility, and less fatigue. In balloons, it means the same degree of expansion for a lower air pressure; other articles benefit, depending on their nature and usage. The production of a lower modulus rubber vulcanizate has been found to be independent of the vulcanizing system, and not to affect substantially the other stress-strain properties such as tensile strength at break, elongation at break, tear strength, etc. The reduced modulus is seen in any product which is made completely or largely from natural latex con-

centrate, whatever the system of fabrication. The preferred range of addition for this effect is from 0.10% to 2.25%, by weight of the dry rubber content of the latex, of hydroxylamine hydrochloride or equivalent proportions of hydroxylamine or other acid addition salts thereof.

The addition of hydroxylamine may also be advantageous where the rubber latex is to be used for the manufacture of moulded foam rubber articles. According to normal commercial practice, the latex concentrate either alone or in blends with synthetic latex is foamed up by mechanical beating to incorporate air or through the release of gas by chemical means such as yeast/hydrogen peroxide (the former being the most common method). The liquid foam is then mixed with

the vulcanizing system, if this has not yet been incorporated, together with fillers, extending oils, protective systems, pigments, adding finally the delayed action gellant, which is commonly sodium silicofluoride. The foamed latex is then poured into the moulds and these are closed. After a suitable time the latex foam gels, and the mould can then be heated to effect vulcanization. This is frequently done by steam heating at 100°C. After this, the moulds are opened, the foam sample removed, washed, and dried.

Because of the water present in the latex foam, the final dried product will be smaller than the original mould size and this is referred to as the volume shrinkage of the mould. Thus,

$$\text{volume shrinkage} = \frac{\text{volume of dry vulcanized foam rubber sample}}{\text{volume of mould used to prepare it}}$$

For a given product size, the mould must be made larger to allow for the volume shrinkage.

It is common knowledge that foam rubber prepared from 100% natural rubber latex has a higher volume shrinkage than that prepared from synthetic rubber latex and that blends of natural and synthetic latices give volume shrinkage values pro-rata the proportion of natural to synthetic latex in the blend. This means that a manufacturer has to use moulds which give the right product size relating to the latex or latex blend according to the volume shrinkage. Alternatively, a manufacturer of a mould foam rubber product of fixed dimensions wishing to change from 100% synthetic rubber latex to 100% natural rubber latex, or to increase the proportion of natural rubber latex in foams made from blends of latices can only do so by changing the mould sizes. This step involves considerable financial outlay.

The treated latex concentrate used in this invention to prepare foam rubber by the conventional method described above, gives a lower volume shrinkage than untreated latex. The latex may be matured or immatured before being foamed. Other properties of the foam

rubber prepared from the treated latex are found to be satisfactory. The preferred range of addition for this effect is from 0.25% to 0.5%, by weight of the dry rubber content of the latex, of hydroxylamine hydrochloride or equivalent proportions of hydroxylamine or other acid addition salts thereof.

These effects are seen, not only when the natural rubber latex is used alone, but also when the latex is a constituent part of a blend of natural and one or more synthetic rubber latices.

The invention is illustrated by the following examples. Parts and percentages are by weight unless otherwise stated.

Example 1

A sample of field latex was centrifuged to give a concentrate of 60% dry rubber content preserved with 0.7% ammonia according to common commercial practice.

Immediately after centrifuging, the concentrate was divided into two parts. One part was the control while one part was treated with 0.15% on the dry rubber content of hydroxylamine hydrochloride added as a 20% solution.

Each sample was compounded as follows:—

Latex	100.0 parts by weight dry rubber
Zinc oxide	1.0 part by weight
Sulphur	1.0 part by weight
Zincdiethyldithiocarbamate	1.0 part by weight

A film of latex was cast onto flat level glass plates to give a sheet of rubber 0.1 cm thick

on drying. When dry, the sample was vulcanized at 100°C. for 30 and 60 minutes.

After vulcanization, the stress-strain properties were determined according to British Standard 903. The results are given in the table below:—

Time of vulcanization at 100 °C.	Control latex		Treated latex	
	30 mins.	60 mins.	30 mins.	60 mins.
Tensile strength, kg/cm ²	183	218	217	170
Elongation at break %	725	745	760	750
Modulus at 500% extension kg/cm ²	30	27	24	22
Relaxed modulus at 100% extension kg/cm ²	6.1	6.0	5.2	4.9

A modulus reduction of between 15% and 20% is seen in the vulcanizate prepared from the treated latex compared to the untreated one.

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Example 2

A sample of field latex was centrifuged to give a concentrate of 60% dry rubber content preserved with 0.20% ammonia and 0.27% sodium pentachlorophenate. The concentrate

was divided into two parts. One part was the control. The second part was treated with 0.15% on the dry rubber content of hydroxylamine hydrochloride immediately after centrifugation. The latex was compounded and processed as for Example 1 and the vulcanizates' properties determined.

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These are given in the table below:—

Time of vulcanization at 100 °C.	Control latex		Treated latex	
	30 mins.	60 mins.	30 mins.	60 mins.
Tensile strength kg/cm ²	166	173	163	193
Elongation at break, %	765	785	775	775
Relaxed modulus at 100% extension kg/cm ²	5.3	5.3	4.5	4.8

25 A reduction in modulus of 10% to 15% is seen in the vulcanizate prepared from the treated latex compared to the control latex.

Example 3

A sample of field latex was centrifuged to give a 60% rubber content latex and divided

into three portions. Portion I was the control, while portions 2 and 3 were treated with 0.10% and 0.25% of hydroxylamine hydrochloride immediately after concentrate preparation.

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Vulcanizates were prepared from dried down films of the latices compounded as follows:—

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40	Latex	100.0 parts by weight dry rubber
	Zinc oxide	1.0 part by weight
	Zinc diethyldithiocarbamate	1.0 part by weight
	Sulphur	0.5, 1.0, 2.0, 3.0 parts by weight

Vulcanization was effected at 100°C. for 15 minutes and the relaxed modulus at 100% extension determined. Results are given in kg/cm².

Sulphur content (parts by weight)	Control latex	Latex + 0.10% hydroxylamine hydrochloride	Latex + 0.25% hydroxylamine hydrochloride
0.5	6.3	5.5	2.2
1.0	7.4	7.2	2.4
2.0	9.9	9.1	6.4
3.0	12.2	11.4	7.5

Modulus is seen for the vulcanizates from the treated latices of between 3% and 68% compared to the untreated latex.

Example 4

10 A bulk of field latex was concentrated by centrifugation to give 60% dry rubber content concentrate preserved with 0.7% ammonia.

It was divided into three parts. Part one was the control, while parts two and three were treated respectively with 0.25% and 0.50% by weight of hydroxylamine hydrochloride on the dry rubber content of the latex.

Foam samples were prepared without filler and without maturation according to the following formula:—

25	Latex	100.0 parts by weight dry rubber
	Zinc oxide	5.0 parts by weight
	Sulphur	2.5 parts by weight
	Zinc diethyldithiocarbamate	0.8 part by weight
	Zinc mercaptobenzoethiazole	0.4 part by weight
	Antioxidant	1.0 part by weight
	Potassium oleate	1.0 part by weight
	Trimene* base	1.0 part by weight
30	Sodium silicofluoride	1.2 to 5.0 parts by weight
	*Trimene is a Registered Trade Mark.	

35 The latex system was 100% natural rubber latex, 75% natural rubber latex + 25% styrene/butadiene polymer latex and 100% styrene/butadiene latex each % referring to the proportion of dry rubber in the system.

The volume shrinkage was determined on samples of foam after vulcanization for 30 minutes at 100°C. and drying for 16 hours at 70°C.

	Foam Properties	
	Density Gms/cc.	Volume % shrinkage
Untreated latex (100%)	0.144	18.1
Untreated latex (75%) + 25% synthetic latex	0.107	14.0
100% synthetic latex	0.107	9.4
0.25% hydroxylamine treated latex (100%)	0.131	14.8
0.25% hydroxylamine treated latex (75%) + 25% synthetic latex	0.108	12.1
0.5% hydroxylamine treated latex (100%)	0.118	15.1
0.5% hydroxylamine treated latex (75%) + 25% synthetic latex	0.108	10.9

A shrinkage reduction of between 14% and 22% is seen for foam prepared from the treated latices compared to the untreated ones.

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Example 5

A bulk of field latex was centrifuged to give a 60% dry rubber content latex preserved with 0.7% of ammonia. The latex was divided into two parts—part one was untreated, while
10 part two was modified by chemical addition

of 0.25% hydroxylamine hydrochloride immediately after concentration.

Foam rubber samples were prepared as in Example 4 except for the fact that the foam rubber was further compounded with 30 parts of whiting per 100 parts of dry rubber. Blends of natural and styrene-butadiene copolymer latices were used.

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The volume shrinkage was as follows:—

	Foam Properties	
	Density Gms/cc.	Volume Shrinkage %
Untreated latex (100%)	0.145	23.4
Untreated latex (75%) + 25% synthetic latex	0.144	18.8
Untreated latex (50%) + 50% synthetic latex	0.137	15.8
Synthetic latex (100%)	0.123	12.5
0.25% hydroxylamine treated latex (100%)	0.137	16.1
0.25% hydroxylamine treated latex (75%) + 25% synthetic latex	0.138	17.0
0.25% hydroxylamine treated latex (50%) + 50% synthetic latex	0.129	14.4

The treated latex gives foams showing a reduction in shrinkage of from 9% to 31% compared to foams prepared from the untreated latex, alone and in blends with synthetic latex.

WHAT WE CLAIM IS:—

1. A process for the manufacture of rubber latex products as hereinbefore defined characterised in that the rubber latex used in the manufacture has been treated by adding hydroxylamine or an acid addition salt thereof to the rubber latex concentrate.

2. A process as claimed in Claim 1 wherein the addition of the hydroxylamine or acid addition salt thereof has been made substantially immediately after concentration of the latex.

3. A process as claimed in either Claim 1 or Claim 2 wherein the hydroxylamine is present in a concentration of from 0.05% to 2.0% by weight on the weight of the dry rubber content of the latex.

4. A process as claimed in any one of Claims 1 to 3 wherein the product is a vulcanized rubber latex product having a reduced modulus (compared to a product made using untreated latex concentrate) and wherein the amount of hydroxylamine or acid addition

salt thereof present is from 0.10% to 0.25% by weight on the dry rubber content of the latex.

5. A process as claimed in any one of Claims 1 to 3 wherein the product is a moulded foam rubber product having a reduced volume shrinkage (compared to a product made using untreated latex concentrate) and wherein the amount of hydroxylamine or acid addition salt thereof present is from 0.25% to 0.50% by weight on the dry rubber content of the latex.

6. A process as claimed in any one of Claims 1 to 5 wherein the rubber latex is a blend of natural rubber latex concentrate and one or more synthetic polymer latices.

7. A process as claimed in any one of Claims 1 to 6 and substantially as described in any one of Examples 1 to 5.

8. Rubber latex products whenever formed by the process claimed in any one of Claims 1 to 7.

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	Foam Properties	
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Untreated latex (75%) + 25% synthetic latex	0.144	18.8
Untreated latex (50%) + 50% synthetic latex	0.137	15.8
Synthetic latex (100%)	0.123	12.5
0.25% hydroxylamine treated latex (100%)	0.137	16.1
0.25% hydroxylamine treated latex (75%) + 25% synthetic latex	0.138	17.0
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15 addition salt thereof has been made substantially immediately after concentration of the latex.

3. A process as claimed in either Claim 1 or Claim 2 wherein the hydroxylamine is
20 present in a concentration of from 0.05% to 2.0% by weight on the weight of the dry rubber content of the latex.

4. A process as claimed in any one of
25 Claims 1 to 3 wherein the product is a vulcanized rubber latex product having a reduced modulus (compared to a product made using untreated latex concentrate) and wherein the amount of hydroxylamine or acid addi-

tion salt thereof present is from 0.10% to 30 0.25% by weight on the dry rubber content of the latex.

5. A process as claimed in any one of Claims 1 to 3 wherein the product is a moulded foam rubber product having a reduced volume shrinkage (compared to a product made using
35 untreated latex concentrate) and wherein the amount of hydroxylamine or acid addition salt thereof present is from 0.25% to 0.50% by weight on the dry rubber content of the latex.

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