

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Stabilisation of Natural Rubber.

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 declare the invention (a communication from Balachandra Chakkingal Sekhar, a Malayan Subject, of The Rubber Research Institute, of Malaya, 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 is for improvements in or relating to the stabilisation of natural rubber and is concerned with the treatment of rubber latex to produce a rubber which has improved storage properties.

It is well known that natural rubber derived from *Hevea Brasiliensis* latex undergoes hardening, i.e. loss of plasticity, during shipment and storage. This plasticity change can be of the order of 10–40 Mooney viscosity units increase. This variable change in hardness of the rubber has made it impossible up to the present time to include a value for plasticity in the technical classification of rubber, a desirable factor for competition with man-made rubbers which are more uniform in this respect. The present invention has for an object to control the plasticity changes on storage of natural rubber to the advantage of the natural rubber industry.

The hardening of rubber on storage has, in the past, been ascribed to mechanisms,

such as cross-linking, caused by peroxidic or other free-radical forming groups or to changes in non-rubbers present in rubber. We have found, however, that even rubber from latex collected under nitrogen undergoes storage hardening. We have also shown that the cross-linking reaction referred to here is not a free radical process but an ionic one. By a series of investigations, we have come to the conclusion that the polyisoprene molecule in *Hevea* latex contains carbonyl and/or carboxylic groups. These groups, under dry conditions, either condense and combine with each other inter- or intra-molecularly, or combine with each other in a similar manner through polyfunctional amines or other like molecules naturally present in latex. This inter- or intra-molecular reaction, we believe, causes the phenomenon of storage hardening in natural rubber. As would be expected, with such reactions between carbonyl groups, the hardening of the rubber is catalysed by strongly alkaline or polar substances such as caustic alkali, alkali metal cyanides or nitrobenzene. We have employed a special accelerated test method for estimating the storage hardening properties of natural rubber. This consists in heating 50 gms. of the rubber in the form of crepe, sheet or film in a desiccator at 144° F. for 48 hours over phosphorus pentoxide and in vacuum. Under such conditions, normal rubber will have a Mooney viscosity increase of 50 to 100%. All hardening data quoted in the following tables were determined by this test method unless otherwise stated.

[Price 4s. 6d.]

TABLE 1.

To different portions of the same field latex is added 0.5% by weight (based on the rubber solids content) of potassium cyanide, potassium hydroxide and nitrobenzene. Films were prepared from these latices and the Mooney viscosity determined before and after accelerated storage.

Table 1 gives the results:—

Sample	Mooney Viscosity		
	Before storage but after treatment	After accelerated storage	% increase during accelerated storage
Control	48	67	40
Potassium cyanide	52	110	112
Potassium hydroxide	54	90	67
Nitrobenzene	58	102	76

Organic amines are known to be particularly reactive towards carbonyl groups and we believe that this provides an explanation of the known cross-linking resulting in the immediate hardening of natural rubber to which certain polyfunctional amines, notably the *m*- and *p*-phenylene diamines, benzidine, diaminophenols and hydrazine salts, have been added. Supporting evidence is found in the known fact that similar addition of ortho-phenylene diamine results in only a small amount of hardening, the steric hindrance of the second amine group apparently effectively preventing its participation in the reaction essential for the formation of an effective cross-link.

When the oxygenated functional groups (e.g. carbonyl or carboxyl) of rubber have fully reacted with polyfunctional amines, their ability to participate in further cross-link formation would be expected to be substantially reduced and we have indeed found that rubber which has been treated with such amines shows much reduced hardening in our accelerated storage test. These observations, however, are of little value in controlling the hardening of rubber occurring during shipment, since the rubber has initially been so greatly hardened that its processability may be impaired.

We have now made the important discovery that many mono-functional amines are capable of reaction with the reactive groups responsible for the spontaneous hardening of natural rubber without causing any objectionable initial increase in hardness of the rubber but in a manner such as to suppress any further tendency to cross-link on storage.

According to the present invention, therefore, there is provided a method of stabilising natural rubber against undesirable hardening on storage which comprises adding to rubber latex a derivative of ammonia of the general formula XNH_2 , wherein X is a hydroxy group, a hydroxy-alkyl group or an aromatic nucleus free from any basic group or basic substituent. The above-mentioned ammonia derivatives may be added to field latex or to a preserved and/or concentrated latex. The amount of the ammonia derivative added to the latex is preferably between 0.1% and 5% by weight of the rubber solids in the latex.

The present invention, by the addition of one of the said derivatives of ammonia, modifies the cross-linking ability of the rubber latex before its manufacture into sheet crepe or other form of solid rubber and thereby prevents any appreciable hardening on storage of the rubber, while at the same time avoiding any marked initial hardening of the rubber, thus preserving its initial softness which is a great advantage in facilitating the methods of mixing and compounding employed in the rubber manufacturing industry.

The following examples will serve to illustrate the manner in which the invention may be carried into effect.

EXAMPLE 1.

A natural rubber latex was treated with 0.5% and 1% of hydroxylamine by weight of the rubber solids before coagulation and sheeting. The dry sheets were stored at ambient temperature and tested for Mooney viscosity at intervals. Table 2 gives the results obtained.



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TABLE 2.

Hydroxylamine added			Mooney Viscosity after Storage			
			0 days	32 days	75 days	Accelerated storage
5	Nil (control)	...	40	44	49	62
	0.5%	...	39	38	39	42
	1.0%	...	39	39	38	40



accelerat

10 It is evident from the results that the additions of hydroxylamine, as compared with the control, prevented the rubber from hardening.

thylamine by weight of the rubber solids was added prior to coagulation and sheeting. The resulting sheets were dried in the usual manner and stored at ambient temperatures. The Mooney viscosity of the rubber was determined at frequent intervals and is given in Table 3. 15 20

EXAMPLE 2.

To field latex 0.5% and 1.0% of naph-

TABLE 3.

Naphthylamine added			Mooney Viscosity after Storage			
			0 days	32 days	75 days	Accelerated storage
25	Nil (Control)	...	40	44	49	62
	0.5%	...	55	54	54	57
	1.0%	...	53	50	50	55

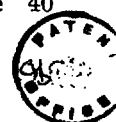
EXAMPLE 3.

30 The results given above clearly demonstrate that the additions of naphthylamine inhibited cross-linking, hence hardening, of the rubber on storage as compared with the untreated (control) rubber.

Field latex was treated with 0.5% and 1.0% of ethanolamine by weight of the rubber solids and the Mooney viscosity of the dry sheets before and after normal and accelerated storage determined. These are given in Table 4. 35 40

TABLE 4.

Ethanolamine added			Mooney Viscosity after Storage		
			0 days	80 days	Accelerated storage
45	Nil (Control)	...	34	40	64
	0.5%	...	34	36	40
	1.0%	...	33	34	39



storage

EXAMPLE 4.

50 Field latex was treated with 0.5% of aniline by weight of the rubber solids and the Mooney viscosity of the dried sheets produced from the latex before storage was 56, the figure rising only to 58 after accelerated storage as above described.

are the values obtained using the small rotor. 60

WHAT WE CLAIM IS:—

1. A method of stabilising natural rubber against undesirable hardening on storage which comprises adding to natural rubber latex a derivative of ammonia of the general formula XNH_2 , wherein X is 65

The figures for Mooney viscosity quoted in the foregoing description and examples



Examples

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	1.0%	...	53	50	50	55

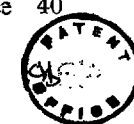
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* C L M S *



Examples

a hydroxy group, or a hydroxyalkyl group or aromatic nucleus free from any basic group or basic substituent.

2. A method according to Claim 1 in which said ammonia derivative is monoethanolamine.

3. A method according to Claim 1, in which said ammonia derivative is naphthylamine or aniline.

4. A method according to Claim 1 in which said ammonia derivative is hydroxylamine.

5. A method according to any of the preceding claims, wherein said ammonia derivative is employed in an amount of

from 0.1% to 5% by weight of the rubber solids content of the latex.

6. The method of stabilising natural rubber against hardening on storage by the addition of a derivative of ammonia substantially as described in any of Examples 1 to 4.

7. Natural rubber when stabilised by the method claimed in any of the preceding claims.

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