

PATENT SPECIFICATION

(11) 1 373 630

1 373 630

- (21) Application No. 61880/70 (22) Filed 31 Jan. 1971
 (23) Complete Specification filed 31 Jan. 1972
 (44) Complete Specification published 13 Nov. 1974
 (51) International Classification C08C 11/04
 (52) Index at acceptance
 C3Q C11 C15 C17 C2 C6A C8C D1A S2 T2A
 (72) Inventor SIN SIEW WENG

(19)



(54) IMPROVEMENTS IN OR RELATING TO THE STABILISATION OF NATURAL RUBBER

(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:—

This invention is for improvements in or relating to the stabilisation of natural rubber and is concerned with the treatment of solid rubber to produce a raw rubber or semi-manufactured rubber which has improved storage properties.

It is well known that natural rubber derived from *Hevea brasiliensis* latex undergoes hardening, i.e., increase of viscosity during processing, shipment and storage. This change can be of the order of 10—40 Mooney viscosity (ML 1+4 at 100°C) increase. Up to 1966 this variable change in hardness of the rubber made it impossible to include a value of viscosity in the technical classification of rubber. Synthetic rubbers are specified in this respect. The tendency for natural rubber to harden on storage is not limited to rubber in its raw state, but also exists in its premasticated and compounded form. It has recently been shown that the rate of storage hardening is greatly increased when the rubber has been subjected to some form of heat treatment as in premastication and/or mixing in an internal mixer.

A known method of stabilising natural rubber against undesirable hardening on storage is by adding to natural rubber latex a derivative of ammonia of the general formula XNH_2 wherein X is a hydroxyl group, a hydroxyalkyl group or an aromatic nucleus free from any basic group or basic substituent. This method is covered by British Patent Specification No. 965,757. It is capable of yielding natural rubber with stabilised vis-

[Price 25p]

cosity and is consequently widely used in the preparation of Standard Malaysian Rubber (SMR) 5CV and 5LV grades, but it will be appreciated that the method is restricted to rubbers available in a form such as fluid latex which can be treated with aqueous solutions of the additive. Furthermore as rubber is stabilised essentially at the viscosity with which it leaves the tree and since this viscosity is dependent on clone, age of tree and other factors, it has been found from experience that it is impractical to produce all viscosity stabilised rubbers at one viscosity level. Consequently commercial rubbers stabilised according to Specification No. 965,757, are presently marketed at several viscosity levels, e.g.

		ML 1+4 at 100°C	
SMR 5CV	50	50±5	
	CV 55	55±5	
	CV	60±5	
	CV 65	65±5	65
	CV 70	70±5	
SMR 5LV	45	45±5	
	LV	50±5	
	LV 55	55±5	
	LV 60	60±5	70
	LV 65	65±5	

The present invention provides a method of treating natural rubber to stabilise it against undesired hardening on storage, which method comprises adding to natural rubber in the solid state hydroxylamine or an acid addition salt thereof.

The rubber is used in the solid state. It may take the form of dry rubber or of wet coagula. It may comprise natural rubber from any source, and may optionally contain a proportion of synthetic rubbers. The rubber may be treated in a compounded or an uncompounded state. In those cases when the rubber is to be compounded a substantial time before being vulcanised, it may be convenient

to add the hydroxylamine with the other additives during compounding is used and tyre retread compound production often takes place long before the compound is used and vulcanised, so that the rubber in such tyre retread compounds may advantageously be treated according to this invention.

The hydroxylamine may be added to the rubber either as a master batch in rubber, or in solution or dispersion in an appropriate fluid or, more preferably when dry rubber is being treated, dry. We have found it convenient to use hydroxylamine in the form of its neutral sulphate. The amount of hydroxylamine used is preferably from 0.01% to 0.5%, particularly from 0.05% to 0.15%, by weight on the weight of the dry rubber. The effect obtained using less than 0.01% of hydroxylamine may be so small as to be scarcely noticeable. While there is no critical upper limit on the amount of hydroxylamine which may be used, little or no advantage accrues from using more than 0.5%.

Dry rubber and the added hydroxylamine need to be mixed and are preferably also subjected, during or after mixing, to an elevated temperature. These two requirements can conveniently be met by performing the mixing operation in an internal mixer (e.g. a Banbury mixer) or in some other mixing apparatus in which elevated temperatures are developed. Suitable mixing times will generally be in the range of 1 to 10 minutes.

The elevated temperature to which the dry rubber is subjected during or after mixing is preferably at least 100°C. The temperature must not, however, be so high that either the rubber undergoes thermal decomposition, or (when vulcanizing ingredients are added to the mix) premature vulcanization takes place. We have found that the use of Banbury mixers with rotor and jacket starting temperature of from 100°C to 120°C is satisfactory and results in stock dump temperatures in the range 150°C to 180°C.

The viscosity level of the treated rubber can be controlled to a desired value by suitable adjustment of the amount of hydroxylamine added and of the temperature and time of mixing. Other things being equal; a larger amount of hydroxylamine reduces the viscosity; a higher temperature in the mixer reduces the viscosity; a longer mixing time reduces the viscosity.

When the rubber is in the form of wet coagula, the hydroxylamine may conveniently be added during creping. The hydroxylamine may be either in the dry form, or as a solution, e.g. a 20% by weight aqueous solution of hydroxylamine neutral sulphate, or more preferably in the form of a latex coagula masterbatch. The masterbatch may then be blended with the coagula, preferably in a weight ratio (wet coagula to latex coagula masterbatch) of from 25:75 to 90:10.

Wet coagula are conveniently treated according to this invention at ambient temperature, or at the slightly elevated temperatures (3° to 6°C above ambient) generally generated during the creping operation. There is, however, no reason why the treated rubber should not be heated at temperatures up to 60°C or above during or after creping. Indeed, the treated rubber will normally be crumbled and dried at an elevated temperature.

The method of the present invention offers the following advantages over the latex treatment method described in Specification No. 965,757, though it should be understood that these advantages are not necessarily realised in every case. By the method of the present invention, it is possible

(a) to produce viscosity stabilised rubber from solid natural rubber of any origin,

(b) to produce viscosity stabilised rubber at any desired viscosity and at only one level of viscosity if required.

(c) to produce viscosity stabilised rubber with a more efficient use of additive since none of the water-soluble chemical agent is lost during processing,

(d) to apply this viscosity stabilising principle to dry compounding such as in retread compound production, or to other rubber compound production wherein it is desirable that the final compound should maintain its viscosity on storage.

We have employed a method for estimating the storage hardening properties of natural rubber which is already used widely for testing CV/LV rubbers. This involves exposing the sample to conditions which cause an acceleration of the storage hardening process. The test is to make measurements of the Wallace rapid plasticity of standard test pieces before (P_0) and after (P_h) 24 hours storage over phosphorus pentoxide at atmospheric pressure at 60°C. Under such conditions unstabilised rubbers will have a plasticity change of about 30 Wallace Plasticity units whereas viscosity stabilised rubbers show changes in viscosity of 8 units or less. Measurements were also made (P_{30}) of the plasticity after ageing for 30 minutes in an oven at 140°C.

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

EXAMPLE 1.

A dry SMR 5L rubber was mixed with 0.0, 0.05, 0.10 and 0.15 p.h.r. hydroxylamine neutral sulphate in a Banbury (00 C model, rotor speed 80 r.p.m.) for 2, 3 and 4 minutes mixing time at two rotor/jacket starting temperature of 100°C and 120°C Hydroxylamine neutral sulphate was added in the form of a 50 hydroxylamine neutral sulphate: 50 SMR 5CV masterbatch together with the rubber samples at the start of the mixing cycle. Properties examined besides Accelerated

Storage Hardening (ΔP) were Plasticity Retention Index (PRI) and normal storage hardening (stored at $20 \pm 2^\circ\text{C}/65 \pm 5\%$ Relative Humidity) as measured by Mooney viscosity over a period of 90 days. Details of mixing including stock dump temperature, peak power, total energy consumption and the test results on the rubbers are given in Table 1.

It is evident from the results that the additions of hydroxylamine prevented the rubber from hardening. The results above also demonstrate that

(a) the rate of the stabilising reaction of hydroxylamine on rubber is temperature dependent,

(b) the amount of hydroxylamine neutral sulphate needed for viscosity stabilisation can be appreciably lower than that required for conventional latex CV rubber production in which aqueous solutions are employed,

(c) PRI is hardly affected by the heat treatment adopted,

(d) hydroxylamine has a peptising effect on natural rubber; this may be exploited to advantage when high viscosity raw materials are encountered,

(e) as there is a choice of raw materials, mixing conditions and amount of hydroxylamine added, the viscosity of the final rubber can be adjusted to any desired value.

20

25

30

TABLE 1—Dry Viscosity Stabilisation

Sample Ref.	Banbury (OOC Model, 2000 ml, 80 rpm rotor speed)				Stock Dump temp. (°C)	P ₀	P ₈₀	PRI (%)	P _h	ΔP	Mooney Viscosity ML 1+4 at 100°C.		
	Rotor & Jacket temp. (°C)	Mixing time (mins)	Peak Power (KW)	Total Energy Con- sumption (KWH)							Initial	30 days	90 days
Control SMR 5L						57	54	95	87.0	30	76	75	76½
Control SMR 5CV						38	33.5	88	40.5	2.5	61	61	61
Control SMR 5L	100	2	16.0	0.41	155	48.0	43.5	91	68.5	20.5	74	77	83½
+0.05 phr HNS	100	2	15.9	0.41	155	45.5	41.0	90	56.5	11.0	72	73½	75
+0.10 phr HNS	100	2	14.1	0.42	156	43.5	37.5	86	48.5	5.0	71	70	71
+0.15 phr HNS	100	2	14.7	0.41	156	42.0	33.5	80	45.0	3.0	69	69	69½
Control SMR 5L	100	3	14.8	0.61	164	42	35.0	83	57.5	15.5	72	82	86½
+0.05 phr HNS	100	3	16.2	0.61	170	37.5	31.0	83	42.5	5.0	67	65	69
+0.10 phr HNS	100	3	17.7	0.62	178	32.5	27.0	83	35.0	2.5	61	60½	61
+0.15 phr HNS	100	3	14.9	0.62	179	33.0	26.0	79	33.5	0.5	61	56½	58
Control SMR 5L	100	4	15.3	0.81	179	35.5	29.0	82	45.0	9.5	64½	77	81
+0.05 phr HNS	100	4	15.8	0.79	179	29.0	25.0	86	32.0	3.0	55½	54	55
+0.10 phr HNS	100	4	13.2	0.79	179	26.5	22.0	83	27.5	1.0	53	52	53
+0.15 phr HNS	100	4	14.0	0.79	179	26.0	22.5	87	27.5	1.5	52½	52	52
Control SML 5L	120	2	12.7	0.45	160	43.0	41.5	97	66.5	23.5	71	75½	81
+0.05 phr HNS	120	2	12.4	0.46	161	43.5	38.0	87	51.5	8.0	72	73	75
+0.10 phr HNS	120	2	13.0	0.41	163	40.0	33.0	83	42.0	2.0	70½	70	71½
+0.15 phr HNS	120	2	13.7	0.40	163	40.0	33.0	83	41.5	1.5	70½	71	71
Control SMR 5L	120	3	13.4	0.58	179	36.0	30.0	83	45.5	9.5	66	80	86½
+0.05 phr HNS	120	3	13.3	0.59	179	33.5	28.0	84	35.5	2.0	61	62	63½
+0.10 phr HNS	120	3	13.3	0.58	179	30.0	25.0	83	30.0	0	58	57½	56
+0.15 phr HNS	120	3	13.7	0.58	179	31.0	25.0	81.0	31.0	0	59	58	60
Control SMR 5L	120	4	13.3	0.77	179	29.0	25.0	86.0	37.5	8.5	55½	68	73
+0.05 phr HNS	120	4	13.6	0.75	179	26.0	21.5	83	28.0	2.0	49½	48½	52
+0.10 phr HNS	120	4	13.4	0.76	179	24.0	20.0	83	25.0	1.0	49	49	50
+0.15 phr HNS	120	4	13.0	0.76	179	25.0	21.5	86	26.5	1.5	48	48	50

Note: HNS denotes Hydroxylamine neutral sulphate.

Details of test methods used are given in Rib. Res. Inst. Malaya SMR Bull. No. 7.

Technological evaluation of dry viscosity stabilised rubber prepared by mixing in the Banbury (OOC Model) for 3 minutes at 120°C Jacket/Rotor starting temperature with 0.10 and 0.15 p.h.r. hydroxylamine neutral sulphate and compared to a control SMR 5CV rubber prepared from the same source of bulked latex and stabilised with 0.15 p.h.r. hydroxylamine neutral sulphate, showed that the rubbers are comparable in technological properties. Details of formulation used, mixing and vulcanisation conditions and test results are given in Tables 2—5.

15

Table 2.
Formulation, mixing and vulcanisation conditions

20

25

30

35

	parts by weight
Rubber	100
IRB-2 HAF Carbon black	45
Durham Noled ZnO	5
Stearic acid	2
Dutrex R	5
Nonox ZA	1.5
Sulphur	2.5
Santocure NS	0.6

'Dutrex', 'Nonox' and 'Santocure' are Registered Trade Marks.
Banbury OOC Model (2000 ml batch volume, 80 r.p.m. rotor speed)
0 minutes: Start clock, add rubber, powders and black+oil.
2 minutes: Sweep down.
3 minutes: Dump.

Vulcanisation
30 minutes at 140°C.

TABLE 3

Technological evaluation of dry viscosity stabilised rubber—raw rubber properties

Sample Reference	SMR-5L +0.1 phr HNS	SMR-5L +0.15 phr HNS	Control SMR-5CV	SMR 5L
Mooney VR (ML 1+4 at 100°C)	65½	67½	62	76
Wallace Plasticity Unaged (P ₀)	30.0	31.0	36.5	52.5
Accelerated Storage Hardening (P _h)	30.0	31.0	42.0	83.0
ΔP	0	0	5.5	30.5

Notes:—HNS denotes hydroxylamine neutral sulphate.

TABLE 4

Technological Evaluation of Dry Viscosity Stabilised Rubber—
Compounding and Curing Characteristics

Sample Reference	5L+0.10 phr HNS	5L+0.15 phr HNS	Control 5CV
Banbury Mixing Details			
Peak Power (KW)	15.7	15.9	14.9
Total Energy Consumption on (KWH)	0.54	0.53	0.50
Dump Temperature (°C)	155	158	155
Mooney Viscometer			
V _B (ML 1+4 @ 100°C)	83	81	82
V _C (ML 1+4 @ 100°C)	55	54	54
Scorch time (min. to 5 pt. rise at 120°C)	19.0	19.5	18.0
Monsanto Rheometer (MP-V Model)			
Starting Conditions HS, Temp. 140°C; Range 100, Chart Motor 60' Preheat 20"			
Minimum Viscosity, T _{min.} (in. lb.)	21.0	21.0	20.8
Scorch Time, t ₂ (min.)	8.3	8.3	7.7
Maximum Torque, T _{max} (in. lb)	65.0	64.8	64.2
Optimum Torque, T ₉₀ (in. lb)	60.6	60.4	59.9
Optimum Cure Time t ₉₀ (min)	28.8	28.3	26.2
Cure rate (t ₉₀ -t ₂) (min)	20.5	20.0	18.5
T _{max} -T _{min.} (ΔT) (in. lb)	44.0	43.8	43.4

'Monsanto' is a Registered Trade Mark.

TABLE 5

Technological Evaluation of Dry Viscosity Stabilised Rubber—Vulcanizate Properties

Sample Reference	Cure Time Min. @30'/140°C	5L+0.10 phr HNS	5L+0.15 phr HNS	Control CV
Tensile Strength (Kg. cm ⁻²)	Unaged	287	278	285
	1d/100°C	216	231	239
	3d/ „	76	64	68
Elongation @ Break (%)	Unaged	490	510	550
	1d/100°C	420	400	400
	3d/ „	180	170	170
Modulus @ 300% (Kg. cm ⁻²)	Unaged	151	134	125
	1d/100°C	154	174	177
	3d „	—	—	—
Relaxed Modulus, MR 100 (Kg. cm ⁻²)		19.1	18.1	18.2
Dunlop Resilience @20°C. (%)		58.4	56.8	59.1
Hardness (IRHD)		66.9	66.1	66.2
Mooney V _e		56	56½	56½
Accelerated ageing (percentage retention)		1 day @ 100°C		
Tensile Strength		75	83	84
Elongation @ Break		86	78	73
Modulus @ 300%		102	130	142

TABLE 5 (continued)

Sample Reference	Cure Time Min. @ 30'/140°C	5L+0.10 phr HNS	5L+0.15 phr HNS	Control CV
Accelerated ageing (Percentage retention)	3 days at 100°C			
Tensile Strength		26	23	24
Elongation @ Break		37	33	31
Modulus @ 300%		—	—	—
Tear Strength (Kg)		35.0	34.1	33.6
Akron Abrasion (ml. loss/1,000 rev.)		0.107	0.104	0.100
Flex Cracking (Kcs to grade C)		80 70	160 180	150 150
Cut Growth (kcs)	2—4 mm 4—8 mm 8—12 mm	4.42 8.92 54.75	4.25 7.88 5.75	4.50 9.50 15.25
Goodrich Flexometer (Heat Build-up)	Stroke=0.200 in. Applied Load=24 lb.			
Starting Conditions				
Temp. (°F) rise after 25 min.	35'	230	229	230
Temp. (°F) rise after 60 min.		237	234	238
Temp. (°F) rise after 180 min.		260	252	265
Dynamic Compression set (%)		26.5	23.5	39.1

EXAMPLE 2.

The use of 0.10 p.h.r. hydroxylamine neutral sulphate in a typical retread formulation using a fresh SMR 5L sample was examined for compound viscosity change on

normal storage over a period of 75 days and for its effect on technological properties. Details of formulation, mixing and vulcanisation conditions and test results are presented in Tables 6 to 10.

Table 6.
Formulation, mixing and vulcanisation conditions

Formulation	Mix A	Mix B
5 Rubber	100.0	100.0
HAF (Acarb)	45.0	45.0
Hydroxylamine neutral Sulphate	—	0.10
Searic acid	1.0	1.0
10 Phenyl- β -naphthylamine	1.0	1.0
Santocure MOR	0.5	0.5
Vulkalent A	0.25	0.25
Renacit 4	0.25	0.25
Dutrex R	5.0	5.0
15 Insoluble S	2.5	2.5
ZnO	5.0	5.0

'Vulkalent' and 'Renacit' are Registered Trade Marks.

Banbury OOC Mixing

0 minutes: Start clock, add rubber powder and black+oil. 20

2 minutes: Sweep down.

3 minutes: Dump.

Vulcanisation

30 and 40 minutes at 140°C.

25

TABLE 7

Raw rubber properties

Sample Reference	SMR-5L		
	initial	1 mth.	2½ mths.
Mooney VR (ML 1+4 at 100°C)	68	71½	74
Wallace Plasticity Unaged (P ₀)	40		
Aged, 30'/140°C (P ₃₀)	39		
PRI %	98		
Accelerated Storage Hardening, P _h	76		
ΔP	36		

TABLE 8

Retread compound—compounding and curing characteristics

Sample Reference	Mix A SMR-5L	Mix B SMR-5L
Banbury Mixing Details Peak Power (KW)	14.9	14.9
Total Energy Consumption (KWH)	0.64	0.62
Dump Temperature (°C)	170	170
Mooney Viscometer V _B (ML 1+4 at 100°C)	96½	89
Scorch time (min. to 5 pt. rise at 120°C)	8.1	8.5

TABLE 9

Storage behaviour of retread compound

Sample Reference	Control Retread Mix (Mix A)	Hydroxylamine treated Retread Mix (Mix B)
	SMR-5L	SMR-5L
Mooney Compound Viscosity (ML 1+4 at 100°C)		
Initial	55½	48½
After 1 week	60	49½
After 2 weeks	63	50½
After 1 month	66	53
After 2½ months	71	56

TABLE 10

Retread Compound—vulcanisate properties (1)

Sample Reference	Cure Time Min. at 140°C.	Mix A	Mix B
		5L	5L
Tensile strength kg.cm ⁻²	30 40	239 243	235 236
Elongation at break %	30 40	480 480	470 460
Modulus kg.cm ⁻²	30 40	137 132	130 136
Dunlop Resilience at 20°C (%)	30 40	63.1 63.0	62.4 61.6
Hardness (IRHD)	30 40	55.9 56.6	55.8 56.4

The results given in Tables 6 to 10 show that the addition of hydroxylamine inhibited hardening of the rubber on storage as compared with the untreated control rubbers. The small Mooney increase observed in the treated mixes is accredited to carbon black structure/gel formation during storage.

EXAMPLE 3:

- 10 Hydroxylamine neutral sulphate was added as a 10% by weight solution to natural rubber latex and the mixture coagulated with 2% by weight formic acid at pH 5.2 to form a masterbatch. Wet coagula cuplump and tree
- 15 lace (CL/TL), were homogenised and creped

(8 passes) with full water on. The hydroxylamine neutral sulphate latex coagula masterbatch was first blended with about half-portion of the CL/TL blanket and then with the remaining half portion by 7—10 passes with minimum washing. The blended mixture was then crumbled with castor oil and dried for about 4 hours at 100°C.

This experiment was repeated using different masterbatches and other conditions. Details of samples and test results are given in Table 11.

It is evident from the results in Table 11 that addition of hydroxylamine inhibited hardening of the rubber.

20

25

30

TABLE 11

Viscosity-Stabilised Wet Coagula

Sample	CL/TL (parts by wt.)	Latex coagula +HNS (parts by wt.)	% HNS on total blend	Mooney Viscosity (MLH4 @ 100°C)	Po	PH	ΔP
1	100	—	—	78.5	45.5	65.0	19.5
2	—	100	—	66.5	40.5	80.0	39.5
3	—	100	0.15	59.0	35.0	38.5	3.5
4	25	75	0.20	60.5	35.0	41.5	6.5
5	25	75	0.30	59.5	35.0	40.0	5.0
6	25	75	0.40	59.5	33.5	36.0	2.5
7	50	50	0.20	63.5	36.0	44.5	8.5
8	50	50	0.30	61.5	36.5	43.0	6.5
9	50	50	0.40	60.0	36.0	41.5	5.5
10	75	25	0.20	64.0	38.0	48.0	10.0
11	75	25	0.30	63.0	37.0	45.0	8.0
12	75	25	0.40	59.5	32.0	37.5	5.5
13	90	10	0.20	64.0	36.5	47.0	10.5
14	90	10	0.30	61.5	34.5	41.5	7.0
15	90	10	0.40	61.0	35.0	41.5	6.5

Notes: 1) HNS denotes Hydroxylamine neutral sulphate

2) Calculations involving CL/TL and latex based on Dry Rubber Content.

WHAT WE CLAIM IS:—

1. A method of treating natural rubber to stabilise it against undesired hardening on storage, which method comprises adding to natural rubber in the solid state hydroxylamine or an acid addition salt thereof.
2. A method as claimed in claim 1, wherein the acid addition salt of hydroxylamine is hydroxylamine neutral sulphate.
3. A method as claimed in either claim 1 or claim 2, wherein the amount of hydroxylamine used is from 0.01% to 0.5% by weight on the weight of the dry rubber.
4. A method as claimed in claim 3, wherein the amount of hydroxylamine used is from 0.05% to 0.15% by weight on the weight of the dry rubber.
5. A method as claimed in any one of claims 1 to 4, wherein the rubber is subjected, either during or after admixture with the hydroxylamine, to an elevated temperature.
6. A method as claimed in claim 5, wherein the natural rubber in the solid state is dry rubber.
7. A method as claimed in claim 6, wherein the rubber is mixed with the hydroxylamine in an internal mixer.
8. A method as claimed in claim 7, wherein the mixing process is carried out for from 1 to 10 minutes under conditions such that the rubber reaches a temperature which is at least

100°C but not so great that thermal decomposition or vulcanization takes place.

9. A method as claimed in claim 1 and substantially as hereinbefore described in Example 1 or Example 2.

10. A method as claimed in any one of claims 1 to 5, wherein the natural rubber in the solid state is in the form of wet coagula.

11. A method as claimed in claim 10, wherein the hydroxylamine is incorporated into the wet coagula during creping thereof.

12. A method as claimed in claim 10 or 11, wherein the hydroxylamine is added to the wet coagula as a latex coagula masterbatch.

13. A method as claimed in claim 12, wherein the proportion by weight of wet coagula to latex coagula masterbatch is from 25:75 to 90:10.

14. A method as claimed in claim 1 and substantially as hereinbefore described in Example 3.

15. Natural rubber when treated to stabilise it against undesired hardening on storage by the method of any one of claims 1 to 14.

For the Applicants,
STEVENS, HEWLETT & PERKINS,
 Chartered Patent Agents,
 5 Quality Court,
 Chancery Lane,
 London, WC2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
 Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

