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(54) TREATMENT OF NATURAL RUBBER

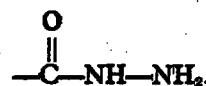
(71) We, THE BOARD OF THE RUBBER RESEARCH INSTITUTE OF MALAYSIA, a Malaysian Body Corporate, of 260 Jalan Ampang, Kuala Lumpur, Malaysia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is well known that natural rubber derived from *Hevea Brasiliensis* latex undergoes hardening i.e. loss of plasticity, during shipping and storage. This hardening is believed to be a result of cross linking between the isoprene chains of natural rubber caused by the reaction of aldehyde and ketone groups attached to the chain with polyamino compounds present in the rubber. Various chemical techniques have been developed to prevent this hardening. One which has had considerable success is the addition of hydroxylamine to the rubber latex before coagulation. The hydroxylamine is believed to react with the carbonyl groups in the rubber and thus prevents cross linking and consequent hardening, vide British Patent No. 965,757. The use of hydroxylamine has enabled rubber of low and constant viscosity to be marketed and has substantially improved the commercial acceptability of natural rubber vis a vis synthetic rubbers. However, the technique is not entirely satisfactory as hydroxylamine is rather volatile and toxic and is not very compatible with the rubber. Also hydroxylamine treatment does not produce reliable viscosity stabilisation, and may fail altogether when used in conjunction with enzyme digestion for the production of deproteinised natural rubber.

The present invention accordingly provides a method of reducing storage hardening in natural rubber comprising admixing with fresh natural rubber one or more organic acid hydrazide(s) in an amount effective to reduce storage hardening.

The term "fresh natural rubber" as used herein means natural rubber in any form e.g. field, creamed or concentrated latex, coagulum or solution, in which the natural rubber has undergone substantially no storage hardening.

The acid hydrazides employed in this invention are restricted to those which contain the group



Further, they contain only one such group per molecule because bi- and polyfunctional compounds can increase the effective viscosity rather than decrease it. The preferred acid hydrazides are those of the medium and long chain fatty acids containing from 8 to 30 carbon atoms per molecule. The organic group may be aliphatic, alicyclic or aromatic, but preferably should not have any substantial proportion of ethylenic unsaturation. The use of branched-chain aliphatic acids is advantageous in promoting compatibility with natural rubber. As will be appreciated, short-chain acids may not be very compatible with the rubber, while the use of very long-chain acids requires the addition of a large amount of compound per active hydrazide group. The precise nature of the acid is not critical to the invention and mixtures of acids may be used. Particularly preferred on account of their structure, cost and ready availability, are the mixture of aliphatic and alicyclic acids known as naphthenic acid.

The production of organic acid hydrazides is straight forward, and may be effected simply by warming together a mixture of the organic acid and hydrazine.

The acid hydrazides can reduce storage hardening in concentrations as low as 0.05 parts by weight per 100 parts by weight of dry rubber (phr). Increasing the quantity of addition to above 5 phr produces only slight extra benefits. The preferred range of addition is from 0.1 phr to 1 phr. The preferred level of hydrazide depends to some extent on molecular weight. 2-Ethylhexanoic hydrazide attains its full effect at about 0.1 phr whereas naphthenic acid hydrazide attains its full effect at about 0.25 phr.

The addition of the hydrazide may be made

at any convenient time to latex or to fresh coagulum. Addition of the acid hydrazide is preferably made to the rubber latex, the lipophilic nature of the acid hydrazide ensuring that it is largely adsorbed on to the dispersed rubber particles. The acid hydrazide may be added as such, or more preferably as an aqueous solution, emulsion or dispersion and dispersed in the latex by stirring. 2-Ethylhexanoic hydrazide is moderately soluble in water and can conveniently be added to latex as an aqueous solution. The addition may be made to field latex, to concentrated or creamed latex or to latex prior to enzyme digestion for production of deproteinised rubber. The hydrazide can be added to coagulated rubber in any suitable form e.g. as a solid or in solution in an organic solvent and the addition can be effected by any convenient method, e.g. on a mill or with the rubber in solution in an organic solvent.

The acid hydrazides possess some oxidant activity and may, if necessary, be used in conjunction with low concentrations of antioxidants. Any type of antioxidant may be employed, the level used depending on its effectiveness. The better antioxidants, e.g. Agerite White, (N,N' - di - 2 - naphthyl - p - phenylenediamine), Nonox ZA, (N - isopropyl - N' - phenyl - p - phenylenediamine), Nonox CNS (mixture of amine and phenolic antioxidants) and Santovar A (2,5-di-t-amyldiquinone) are effective at concentrations as low as 0.01 phr. The preferred range is 0.05 to 0.5 phr but higher concentrations up to 5 phr may also be employed. The words 'Nonox' and 'Santovar' are Registered Trade Marks. The antioxidant is conveniently added along with the acid hydrazide.

However, trials in Malaysia have shown that addition of antioxidant to maintain the Plasticity Retention Index (PRI) of hydrazide stabilised rubber prepared from fresh field latex may not be necessary.

Organic acid hydrazides, particularly those having large organic groups, e.g. the preferred naphthenic acid hydrazides, are much more soluble in natural rubber than hydroxylamine. Even acid hydrazides having relatively small organic groups, thus having appreciable solubility in water, e.g. 2-ethylhexanoic hydrazide, are more soluble in rubber. This solubility advantage when taken with the superior chemical reactivity of hydrazides means that on a molar basis hydrazides are often as much as 5 to 10 times as efficient as is hydroxylamine. Because they have higher molecular weights this higher molar efficiency does not necessarily result in a higher weight efficiency. 2-Ethylhexanoic hydrazide is of comparable efficiency with hydroxylamine on a weight for weight basis although its molecular weight is about 5 times as great. Naphthenic acid hydrazides are in general somewhat more efficient than 2-ethylhexanoic hydrazide on a

molar basis but their higher molecular weight means that they are usually slightly less efficient on a weight basis. Naphthenic acid hydrazides have superior solubility in natural rubber as compared with 2-ethylhexanoic hydrazide and are available from relatively inexpensive naphthenic acids and are preferred for these reasons.

Additionally, organic acid hydrazides are capable of giving virtually complete protection against age hardening whereas even in very high concentrations hydroxylamine provides only partial protection. The stability of the product, the relatively high molecular weight and the low inherent toxicity all contribute to make the acid hydrazides, particularly those of naphthenic acid very much safer to handle than hydroxylamine. A further advantage gained by the use of acid hydrazide especially naphthenic acid hydrazide rather than hydroxylamine is that the hydrazides produce stabilised raw rubber of lighter colour (5L standard) than does hydroxylamine and cause less discolouration on subsequent heating. The hydrazides also have an activating effect on cure systems which contain little or no sulphenamide accelerator. This activation effect becomes less pronounced as sulphenamide level is increased in the cure system.

The following Preparation, Reaction and Examples illustrate the preparation, reactivity, use and effect of the hydrazides of organic acids.

Preparation.

Carboxylic acid hydrazides can be prepared by well known procedures. The hydrazide from Shell (Registered Trade Mark) naphthenic acid 180 was obtained by mixing the acid (100 g, 0.32 mole) and hydrazine hydrate (96 g, 1.92 mole) and heating the mixture at 150°C for 24 hours. The crude product was cooled to room temperature, diluted with ether and washed with water to remove excess hydrazine. The ether phase was dried and evaporated to give the acid hydrazide as a viscous oil, 94g. Found, N 8.7% by weight; theoretical value, 8.6% by weight. The product was soluble in ether, chloroform, benzene and toluene. The IR spectrum showed absorptions at 9.46 μ (>—H), 6.14 μ and 5.99 μ (amide >C=O and —NH₂) and no absorptions which could be ascribed to free carboxylic acid. The spectrum was very similar to that of analytically pure butyric hydrazide.

Reaction.

Reaction of naphthenic acid hydrazide with butyraldehyde in benzene.

Naphthenic acid hydrazide (0.06M) and butyraldehyde (0.024N) were allowed to react at room temperature in benzene solution for 2 hours in the absence of a catalyst. G.L.C. analysis of the reaction mixture indicated at least 90% reaction of the aldehyde.

Work on the reaction of chemically pure acid hydrazides (butyric hydrazide) using TLC analysis also indicates that reaction with aldehydes is complete within two hours at room temperature in the absence of catalyst. In the presence of acetic acid, reaction appears to be almost instantaneous.

Example 1.

Deproteinised natural rubber which had not undergone appreciable storage hardening was dissolved in toluene and treated, in solution, with naphthenic acid hydrazide. After 64 hours

at room temperature the rubber was recovered by precipitation with methanol and dried in vacuo. The effect of the reagent on storage hardening was assessed by measuring the Wallace Plasticity of the rubber at 100°C (or alternatively, the Mooney viscosity) before and after storage for 24 hours at 60°C over phosphorus pentoxide. The storage hardening is expressed as the increase in Plasticity (ΔP) of the aged sample compared with the unaged sample. The results are summarised in Table I.

TABLE I

Amount of hydrazide (phr)	Initial Plasticity	ΔP
0	35.5	31.5
0.06	37.5	11.5
0.125	39.0	10.0
0.25	37.5	-1.5
0.5	33.0	0.5

Example 2.

Naphthenic acid hydrazide was added on an open mill to deproteinised natural rubber which had not undergone appreciable storage

hardening. The rubber was tested as in Example 1 after 64 hours at room temperature. The results are summarised in Table II.

TABLE II

Amount of hydrazide (phr)	Initial Plasticity	ΔP
0.06	20.5	13.0
0.125	21.5	7.5
0.25	20.0	1.0
0.5	17.5	-3.0

Example 3.

2-Ethylhexanoic hydrazide was added on an open mill to deproteinised natural rubber which had not undergone appreciable storage harden-

ing. The rubber was tested as in Example 1 after 64 hours at room temperature. The results are summarised in Table III.

TABLE III

Amount of hydrazide (phr)	Initial Plasticity	ΔP
0	30	16
0.125	21	0
0.25	27.5	-2
0.5	27	-3

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Example 4.

5 Naphthenic acid hydrazide was diluted with
an equal weight of xylene and the solution was
emulsified in a mixture of water and Nonidet
P40 (2% w/w on hydrazide) ('Nonidet' is
a Registered Trade Mark). Field latex was
10 treated with 0.04% drc of sodium metabi-
sulphite and 0.7% drc of castor oil. The naph-
thenic acid hydrazide emulsion (0.25phr hy-
drazide) was added to the latex prior to
coagulation with 2% w/w formic acid at pH
5. The coagulum was matured for 16 hours
before it was crumbled and the crumbs were
dried by hot air circulation at 100°C. Con-

15 trol SMR 5L and SMR 5CV rubbers were
prepared from the same batch of latex by
standard procedures. The rubbers were tested
for viscosity stabilisation (Mooney viscosity)
and also for curing characteristics and the
physical properties of the vulcanizates. The
20 curing recipes are summarised in Table IV and
the results are given in Table V.

Technological properties of the vulcanizates
before and after ageing for 7 days at 70°C
showed no significant differences between
25 hydrazide stabilised rubber, SMR 5CV and
SMR 5L other than those arising from
differences in modulus.

TABLE IV

	ACS-1 Mix parts by weight	Tread Mix parts by weight
Rubber	100	100
Zinc Oxide	6	4
Stearic Acid	0.5	2.0
HAF Black	—	50
Dutrex R	—	5
Sulphur	3.5	2.5
2-Mercaptobenzthiazole	0.5	—
N-Cyclohexylbenzthiazole-2-sulphenamide	—	0.5
Nonox ZA	—	1.5

TABLE V

	SMR 5L	SMR 5CV	Hydrazide Stabilised Rubber	
Volatile matter (% wt)	0.28	0.27	0.31	
Nitrogen (% wt)	0.32	0.49	0.58	
Ash (% wt)	0.16	0.15	0.19	
Dirt (% wt)	0.008	0.009	0.008	
Colour (Lovibond units)	3.5	5.0	3.5	
Wallace Plasticity	52	46	48	
Plasticity Retention Index (PRI)	87	85	77	
Initial Mooney Viscosity (V_R)	72	66	70	
V_R after 24 hr at 60°C over P_2O_5	29	4	5	
Scorch time (min)	ACS-1 mix	11.5	15.0	9.2
	Tread mix	16.7	19.8	19.5
Monsanto Rheometer maximum Torque, 140°C (1b)	ACS-1 mix	18.0	17.8	20.5
	Tread mix	39.2	38.0	38.3
Monsanto Rheometer cure rate, 140°C ($t_{90}-t_2$, min.)	ACS-1 mix	40.0	40.2	21.2
	Tread mix	17.0	17.6	16.4

"Dutrex" and "Monsanto" are Registered Trade Marks.

Example 5.

5 Napthenic acid hydrazide was emulsified as in Example 4 and added to ammoniated fresh latex containing 0.2% by wt. NH_3 . Enzyme for protein digestion was added and the latex was incubated at 32°C for 48 hours. The

latex was diluted to 3% drc and coagulated with dilute (2% by wt.) phosphoric acid. The coagulum was washed on a crepeing mill and dried for 24 hours at 55°C. The results of accelerated storage hardening tests are summarised in Table VI.

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TABLE VI

Amount of hydrazide (phr)	Initial Plasticity	ΔP
0	52	21
0.063	51	13
0.125	47.5	7.5
0.250	41	-2

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Example 6.

Ammoniated fresh latex containing 0.2% by weight NH_3 was treated with a 2% by wt. aqueous solution of 2-ethylhexanoic hydrazide.

The latex was allowed to stand at room temperature for 16 hours, diluted to 15% drc and coagulated with dilute (2% by wt.) phosphoric acid. The coagulum was washed on a

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crepeing mill and dried at 55°C in an air oven. The results of accelerated storage hardening tests are summarised in Table VII.

TABLE VII

Amount of hydrazide (phr)	Initial Plasticity	ΔP
0	46	28
0.013	42	18
0.025	45	7
0.05	43	8
0.10	43	3
0.25	39	4.5
0.50	39	1

Example 7.

5 Napthenic acid hydrazide was diluted with an equal volume of xylene. Antioxidant Santovar A was added and the solution was emulsified in water. The emulsion was added to ammoniated fresh latex (0.2% by wt. NH_3) and the latex was allowed to stand at room temperature for 16 hours. The latex was diluted to 15% drc and coagulated with dilute (2% wt.) phosphoric acid. The coagulum was washed on a crepeing mill and dried in an

air oven at 55°C. The rubber was tested for accelerated storage hardening as described in Example 3 and for susceptibility to oxidative degradation by measuring the Wallace Plasticity at 100°C after air ageing at 140°C for 30 minutes. The Plasticity Retention Index (PRI) is the Wallace Plasticity at 100°C after ageing expressed as a percentage of the initial Plasticity. The results are summarised in Table VIII.

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TABLE VIII

Amount of antioxidant (phr)	Amount of hydrazide (phr)	Initial Plasticity	ΔP	PRI
0	0	48	39	45
0	0.25	32.5	-6.5	17
0.05	0.25	34	-9	18
0.10	0.25	35	-12	19
0.20	0.25	33	-1	60
0.50	0.25	33	-2	57

Example 8.

30 Napthenic acid hydrazide was diluted with an equal volume of xylene. Antioxidant Nonox ZA was added and the solution was emulsified in water. The emulsion was added to ammoniated fresh latex (0.2% by wt. NH_3) together with enzyme for protein digestion and

the latex was incubated at 32°C for 48 hours. The latex was diluted to 3% drc and coagulated with dilute (2% by wt.) phosphoric acid. The coagulum was washed on a crepeing mill and dried in an air oven at 55°C. The results of accelerated storage hardening and PRI tests are summarised in Table IX.

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TABLE IX

Amount of antioxidant (phr)	Amount of hydrazide (phr)	Initial Plasticity	ΔP	PRI
0	0	50	27	21
0	0.25	41	-2	13
0.25	0.25	31	-1	51

Example 9.

5 Naphthenic acid hydrazide and antioxidant Nonox CNS were added to a benzene solution of deproteinised natural rubber which had not undergone appreciable storage hardening. The

solution was evaporated to dryness under reduced pressure and the rubber was tested for accelerated storage hardening and PRI. The results are summarised in Table X.

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TABLE X

Amount of antioxidant (phr)	Amount of hydrazide (phr)	Initial Plasticity	ΔP	PRI
0	0	36	28	67
0	0.25	37	-6	25
0.05	0.25	34	-1	65

15 Prior United Kingdom Patent Application No. 41428/69, Serial No. 1307678, of the Rubber Research Institute of Malaya describes and claims rubber latex products having improved properties produced from rubber latex which has been treated with hydroxylamine. Treatment of fresh natural rubber latex with an organic acid hydrazide as discussed in the present invention produces similar advantages in rubber latex products made therefrom. Therefore in a subsidiary aspect the present invention provides a method of making rubber latex products which method is characterised in that the latex used has been treated with an organic acid hydrazide.

WHAT WE CLAIM IS:—

1. A method of reducing storage hardening in natural rubber comprising admixing with fresh natural rubber, as hereinbefore defined, one or more organic acid hydrazide(s), as hereinbefore defined, in an amount effective to reduce storage hardening.
2. A method as claimed in claim 1 wherein the amount of hydrazide is from 0.05 to 5 phr.
3. A method as claimed in claim 2 wherein the amount of hydrazide is from 0.1 to 1 phr.
4. A method as claimed in any one of claims 1 to 3 wherein the hydrazide is an aliphatic aromatic or alicyclic acid hydrazide or a mixture thereof.
5. A method as claimed in any one of claims 1 to 4 wherein the hydrazide contains from 8 to 30 carbon atoms per molecule.

6. A method as claimed in claim 5 wherein the hydrazide is one or more naphthenic acid hydrazides.

7. A method as claimed in claim 5 wherein the hydrazide is 2-ethylhexanoic hydrazide.

8. A method as claimed in any one of claims 1 to 7 wherein the hydrazide is substantially free from ethylenic unsaturation.

9. A method as claimed in any one of claims 1 to 8, wherein an antioxidant is admixed with the rubber in addition to the hydrazide.

10. A method as claimed in claim 9 wherein the amount of antioxidant is from 0.01 to 5 phr of antioxidant.

11. A method as claimed in claim 10 wherein the amount of antioxidant is from 0.05 to 0.5 phr of antioxidant.

12. A method as claimed in any one of claims 1 to 11 wherein the hydrazide is admixed with the rubber in the form of solid rubber coagulum.

13. A method as claimed in any one of claims 1 to 11 wherein the hydrazide is admixed with the rubber in the form of a rubber solution.

14. A method as claimed in either claim 12 or claim 13 wherein the hydrazide is added in the form of a solid or in solution in an organic solvent to the rubber.

15. A method as claimed in any one of claims 1 to 11 wherein the hydrazide is admixed with the rubber in the form of a rubber latex.

16. A method as claimed in claim 15

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TABLE IX

Amount of antioxidant (phr)	Amount of hydrazide (phr)	Initial Plasticity	ΔP	PRI
0	0	50	27	21
0	0.25	41	-2	13
0.25	0.25	31	-1	51

Example 9.

Naphthenic acid hydrazide and antioxidant Nonox CNS were added to a benzene solution of deproteinised natural rubber which had not undergone appreciable storage hardening. The

solution was evaporated to dryness under reduced pressure and the rubber was tested for accelerated storage hardening and PRI. The results are summarised in Table X.

TABLE X

Amount of antioxidant (phr)	Amount of hydrazide (phr)	Initial Plasticity	ΔP	PRI
0	0	36	28	67
0	0.25	37	-6	25
0.05	0.25	34	-1	65

Prior United Kingdom Patent Application No. 41428/69, Serial No. 1307678, of the Rubber Research Institute of Malaya describes and claims rubber latex products having improved properties produced from rubber latex which has been treated with hydroxylamine. Treatment of fresh natural rubber latex with an organic acid hydrazide as discussed in the present invention produces similar advantages in rubber latex products made therefrom. Therefore in a subsidiary aspect the present invention provides a method of making rubber latex products which method is characterised in that the latex used has been treated with an organic acid hydrazide.

WHAT WE CLAIM IS:—

1. A method of reducing storage hardening in natural rubber comprising admixing with fresh natural rubber, as hereinbefore defined, one or more organic acid hydrazide(s), as hereinbefore defined, in an amount effective to reduce storage hardening.

2. A method as claimed in claim 1 wherein the amount of hydrazide is from 0.05 to 5 phr.

3. A method as claimed in claim 2 wherein the amount of hydrazide is from 0.1 to 1 phr.

4. A method as claimed in any one of claims 1 to 3 wherein the hydrazide is an aliphatic aromatic or alicyclic acid hydrazide or a mixture thereof.

5. A method as claimed in any one of claims 1 to 4 wherein the hydrazide contains from 8 to 30 carbon atoms per molecule.

6. A method as claimed in claim 5 wherein the hydrazide is one or more naphthenic acid hydrazides.

7. A method as claimed in claim 5 wherein the hydrazide is 2-ethylhexanoic hydrazide.

8. A method as claimed in any one of claims 1 to 7 wherein the hydrazide is substantially free from ethylenic unsaturation.

9. A method as claimed in any one of claims 1 to 8, wherein an antioxidant is admixed with the rubber in addition to the hydrazide.

10. A method as claimed in claim 9 wherein the amount of antioxidant is from 0.01 to 5 phr of antioxidant.

11. A method as claimed in claim 10 wherein the amount of antioxidant is from 0.05 to 0.5 phr of antioxidant.

12. A method as claimed in any one of claims 1 to 11 wherein the hydrazide is admixed with the rubber in the form of solid rubber coagulum.

13. A method as claimed in any one of claims 1 to 11 wherein the hydrazide is admixed with the rubber in the form of a rubber solution.

14. A method as claimed in either claim 12 or claim 13 wherein the hydrazide is added in the form of a solid or in solution in an organic solvent to the rubber.

15. A method as claimed in any one of claims 1 to 11 wherein the hydrazide is admixed with the rubber in the form of a rubber latex.

16. A method as claimed in claim 15

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wherein the latex is a field latex.

17. A method as claimed in claim 15 wherein the latex is a creamed or concentrated latex.

5 18. A method as claimed in any one of claims 15 to 17 wherein the hydrazide is added in the form of a solid or a solution, emulsion or dispersion in water to the latex.

10 19. A method as claimed in any one of claims 1 to 18 and substantially as hereinbefore described in any one of Examples 1 to 9.

20. Natural rubber treated by the method claimed in any one of claims 1 to 19.

21. Rubber latex products whenever made from rubber latex treated by the method 15 claimed in claim 1.

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