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(54) TREATMENT OF 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 relates to natural rubber, both vulcanized and unvulcanized, and to a method of removing protein from natural rubber.

Vulcanizates made from natural rubber have superior properties to those from most synthetic elastomers especially in respect of strength, resilience and creep properties and for this reason are widely used in demanding applications such as heavy duty tyres and engineering (spring) applications.

However, increasingly severe service applications require even higher performance and in the case of springs there is competition from steel which though less desirable in certain respects has little tendency to creep under load.

We have previously described how the properties, notably resilience, creep and set properties, of natural and synthetic rubber vulcanizates can be improved by ensuring that each of the non-rubber ingredients present is either completely insoluble in the rubber, or, if soluble, is present in the vulcanized rubber in a smaller concentration than that which would provide a saturated solution therein.

As normally prepared from field latex natural rubber contains a small but significant concentration of protein, salts and other hydrophilic non-rubbers which absorb water and give rise to a variety of undesirable effects. In particular the vulcanization characteristics (scorch time, rate and state of cure) are excessively dependent on the moisture contained in the compound and the modulus of the vulcanizate will vary with its moisture content.

Both enzyme treatment and displacement of interfacial protein from latex by the use of alkali metal soaps have been used to reduce protein contents of rubber subsequently made from the latex although only with partial success unless repeated and extensive centrifugation with soaps was used.

One disadvantage of this purification procedure is that the alkali metal soaps largely remain (as the free acid) in the coagulum and react with zinc oxide conventionally added as an activator during vulcanization, giving rise to zinc salts in the rubber vulcanizate. The zinc salts formed from conventional alkali metal soaps are sparingly soluble in the rubber and are therefore present in the vulcanizate in supersaturated concentrations.

The present invention provides a method of removing protein from natural rubber, which method comprises incubating natural rubber latex with a proteolytic enzyme at a pH suitable for the enzyme in the presence of a soap to prevent premature thickening or coagulation of the latex and subsequently separating proteinaceous material from the rubber, wherein the acid constituent of the soap is one or more carboxylic acids which form rubber-soluble zinc salts.

The nature of the natural rubber latex which is the starting point of the method of this invention is not critical, provided that it has sufficient stability to withstand the incubation without premature coagulation. It may be a field latex, preferably after concentration by centrifuging, as this preliminary step appears to remove some enzyme inhibitor, or it may be a preserved latex, generally in the form of a concentrate. The nature of the preservative chemical is not critical and generally ammonia is used.

Proteolytic enzymes for use in natural rubber latex are well known. We prefer to use subtilisin or a commercial alkaline protease, because the optimum pH range for these enzymes is on the alkaline side, but other

enzymes may be used. The pH of the latex may be chosen at any value suitable for the enzyme, with the proviso that the pH must not be so low that premature coagulation of the rubber takes place. A convenient pH range for the enzymes mentioned above is from 9.5 to 11. The term "proteinaceous material" is used herein to cover protein and degradation products thereof.

The amount of enzyme may be chosen to obtain a desired rate or degree of proteolysis. We find it convenient to use from 10 to 1000 ppm of active enzyme by weight on the weight of the dry rubber, for example 50 ppm of enzyme for centrifuged latex, or 250 ppm of enzyme for uncentrifuged field latex. Time and temperature of incubation may also be chosen to achieve the desired rate and degree of proteolysis, typical figures being from 12 to 60 hours at from 40° C to 25° C. The action of the enzyme is to degrade and solubilise the protein so as to enable it to be readily separated from the rubber particles.

In order to stabilise the latex in the presence of the proteolytic enzyme, so as to prevent premature thickening or coagulation during incubation, a soap, generally an alkali metal or ammonium soap, is added to the latex. The proportion of the added soap is generally in the range 0.1% to 10% by weight on the dry rubber content of the latex. Below 0.1%, little stabilising effect is obtained, while more than 10% is expensive and may modify the properties of the rubber.

An important feature of the invention lies in the choice of the acid constituent of this soap. We prefer to use one or more branched chain aliphatic or alicyclic carboxylic acids which form rubber-soluble zinc salts. We particularly prefer to use alicyclic carboxylic acids containing one or more cyclopentyl or cyclohexyl rings per molecule, particularly the mixture of such acids which is commercially available as naphthenic acids. Typically, naphthenic acid mixtures have the following characteristics:—

(a) the acids are predominantly mono-carboxylic

(b) the carboxylic groups are generally attached to an alicyclic ring through a chain of up to 5 methylene groups

(c) cyclopentyl rings predominate, but cyclohexyl rings may be present

(d) the alicyclic ring may be alkyl substituted

(e) the number of carbon atoms per molecule ranges from less than 7 to more than 20

(f) the number of rings per molecule ranges from 0 to 7 or more

(g) acid number in the range 150—250

(h) average molecular weight in the range 200—330.

Straight-chain aliphatic carboxylic acids are generally not suitable for use in this inven-

tion because they and their zinc salts are not sufficiently soluble in rubber; branched-chain acids of equivalent molecular weight and their zinc salts are much more rubber-soluble. Aromatic carboxylic acids do not in general form rubber-soluble zinc salts. Ethylenically unsaturated carboxylic acids are generally more rubber-soluble than the corresponding saturated acids; however, since unsaturated acids tend to become bound to the rubber during vulcanization, it may be preferable to use saturated acids.

The carboxylic acid component of the soap must be sufficiently large to stabilise the latex. Generally, this requires an alkyl chain at least 6 carbon atoms, and preferably at least 10 carbon atoms, long. There is no critical upper limit on the molecular weight of the carboxylic acid component of the soap, though the available carboxylic acids mostly have less than 25 carbon atoms per molecule.

After incubation, the proteinaceous material is separated from the rubber. Where a solid rubber is required, this separation may conveniently be effected by coagulation. We prefer to dilute the rubber latex prior to coagulation, preferably to a solids content of from 1% to 30% e.g. 2% to 5% by weight, so as to avoid entrapping proteinaceous material in the coagulum. The more concentrated the latex at coagulation, the greater is the proportion of proteinaceous material entrapped in the coagulum. On the other hand, it is both expensive and difficult to coagulate rubber from a latex which has been diluted to less than 1% by weight solids. Any suitable coagulant may be used; in many cases, phosphoric acid may be preferred owing to the oxidation resistance that it confers on the coagulum.

Where a purified rubber latex is required, the proteinaceous material may be removed by centrifuging.

Natural rubber contains about 2.5% by weight of proteinaceous material. Enzyme-treated rubber contains distinctly less, generally not more than 1.0% of proteinaceous material. Protein content may conveniently be estimated by multiplying the measured nitrogen content of the rubber by a factor of 6.25.

This invention also includes, as a novel material in its own right, natural rubber containing:

(i) not more than 1%, preferably not more than 0.5%, by weight of proteinaceous material based on the weight of natural rubber alone; and

(ii) one or more added carboxylic acids, or salts thereof, which acids form rubber-soluble zinc salts.

It is important that the zinc carboxylate, formed by the reaction, during vulcanization, between zinc oxide and the carboxylic acid,

should be present in the vulcanized rubber in a smaller concentration than that which would provide a saturated solution therein. The concentration of a non-rubber ingredient which is just sufficient to provide a saturated solution of the ingredient in the rubber is hereinafter called the critical concentration. The precise solubility of the zinc salt is unimportant; what is important is that the carboxylic acid should be present in the rubber before vulcanization in such an amount that the concentration of zinc carboxylate in the vulcanizate will be less than critical.

Checking the solubility of an ingredient in vulcanized rubber is not an entirely straight forward matter, but several techniques are available. In some cases, examination of the vulcanized rubber under a microscope reveals insoluble particles; however the particles may be of sub-microscopic size. Another technique is to observe the stiffness of the vulcanized rubber at different temperatures; if the rubber softens on heating, it is likely that insoluble ingredients are present and are becoming solubilised at elevated temperatures; theoretical considerations indicate that a vulcanized rubber should become stiffer on being heated, and this does in fact happen when solubilisation is not taking place. A third technique is to extract thoroughly non-rubbers from the vulcanizate; if the modulus of the rubber is less after extraction than before, it is likely that insoluble ingredients were present; in the absence of insoluble ingredients, the modulus generally rises as a result of extraction of non-rubbers.

Cadmium and lead compounds have been proposed as replacements for the zinc compounds generally used as vulcanization accelerators. Where this specification refers to the use of zinc, it is to be understood that the use of cadmium or lead is also contemplated. The zinc, cadmium and lead salts of any particular carboxylic acid are likely to be either all soluble or all insoluble.

The present invention also includes a vulcanized natural rubber in which:—

(a) there is present not more than 1.0%, preferably not more than 0.5%, by weight of proteinaceous material based on the weight of natural rubber alone;

(b) there is present a zinc, cadmium or lead salt of a carboxylic acid, and

(c) each non-rubber ingredient being either completely insoluble in the rubber, or, if soluble, being present in the vulcanized rubber in a smaller concentration than that which would provide a saturated solution therein.

Of the non-rubber ingredients which are conventionally added to rubber during compounding; filler (e.g. carbon black) is insoluble in the vulcanized rubber, zinc oxide (during vulcanization) forms zinc salts and soaps which are slightly soluble in the vulcanized

rubber; sulphur is incorporated in the cross-links; accelerators are largely decomposed or incorporated in the cross-links, but vulcanization also gives rise to the formation of some zinc salts which are slightly soluble in the vulcanized rubber; and carboxylic (e.g. fatty) acids form zinc soaps which are slightly soluble in the vulcanized rubber. Difficulty therefore arises in respect of the combination of zinc oxide with carboxylic (e.g. fatty) acids, and to a lesser extent with accelerators.

With regard to the carboxylic acid which is conventionally added to natural rubber during compounding, it is preferred according to the present invention that this acid also should be one which forms a rubber-soluble zinc salt. Provided of course that the critical concentration is not exceeded, the proportion of the zinc salt in the vulcanized rubber is not of great importance. We prefer to provide from 0.5 to 10 parts per hundred parts of rubber (phr), particularly from 1 to 5 phr of the zinc salt. Often, the properties of the ingredients in the vulcanizable or vulcanized rubbers of this invention will be conventional, and only the nature of the organic acid present will be unusual. Frequently, in conventional rubber mixes, zinc oxide is used in a stoichiometric excess over organic acid, and the excess remains as an insoluble filler in the vulcanized rubber. Generally the vulcanizable rubber compositions of this invention will contain from 0.25 to 10 phr by weight of zinc, measured as zinc oxide, and from 0.25 to 5 phr by weight of the chosen organic carboxylic acid, either free or as the zinc salt.

The term natural rubber is used herein to include blends of a major proportion of natural rubber with a minor proportion of a synthetic rubber. In the case of such blends, proportions of proteinaceous material are expressed on the weight of the natural rubber component of the blend.

The following Examples illustrates the invention.

Example 1.

Field latex was brought to a pH of 10 with ammonia and lightly centrifuged to remove fine latex particles and bottom fraction which inhibit the enzyme somewhat. About 1% by weight of potassium naphthenate on the dry rubber content (DRC) of the latex was then added to prevent premature thickening due to particle association or premature coagulation. The enzyme (subtilisin) was then added at a concentration of 50 ppm (on DRC) of active enzyme, and the mixture was then incubated for 24 hrs. at about 35° C.

After incubation the mixture was diluted to a low solids content (3% by weight total solids) before coagulation with acid in the normal way to remove hydrolysed prot in fragments and other hydrophilic non-rubbers

which are difficult to remove after coagulation even on extended washing on a crepeing mill.

5 After coagulation the coagulum was creped and dried in warm air in the usual way.

Typical analysis figures are given in Table 1, together with comparable figures for field latex, for mature high-ammonia latex, and for fresh latex concentrate treated with other soaps.

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TABLE I

Experimental Rubber	Treatment	Protein (% drc)	Ash (% drc)
1. Fresh field latex	none	2.5	0.2
2. Fresh field latex	enzyme + potassium naphthenate	0.4	0.13
3. Fresh latex con- centrate	enzyme + potassium naphthenate	0.18	0.05
4. Fresh latex con- centrate	enzyme + potassium laurate	0.20	
5. Fresh latex con- centrate	enzyme + potassium 2-ethyl hexanoate	0.60	
6. Mature HA latex	enzyme + potassium naphthenate	0.20	0.04

15 Potassium laurate is an excellent soap, but zinc laurate is insoluble in natural rubber. Potassium 2-ethyl hexanoate is rather less effective as a soap (presumably because its alkyl chain is only just long enough), but zinc 2-ethyl hexanoate is soluble in natural rubber.

Sample of various coagula were compounded and vulcanized under appropriate conditions to give gum vulcanizates having the properties set out in Table II.

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TABLE II

Formulation	parts by weight		
	(i)	(ii)	(iii)
Dried Coagulum from Experiment 1	100	—	—
Dried Coagulum from Experiment 3	—	—	100
Dried Coagulum from Experiment 4	—	100	—
Zinc oxide	5	5	5
Sulphur	0.8	0.8	0.8
Tetrabutylthiuram disulphide	0.8	0.8	0.8
N-morpholinylbenzthiazole-2-sulphenamide	1.9	1.9	1.9
Lauric acid	—	2.0	—
Zinc 2-ethyl hexanoate	2.0	—	2.0
Properties			
Time to stress relax. 1% on 1 minute value (minutes)	10	3	15000
Rebound resilience (%)	93	92	96
Compression set, 1 day at 70°C (%)	7	12	3

In the stress relaxation test, cured samples were stretched by 100% at room temperature, the tension noted after 1 minute, and the time to reduce that tension by 1% observed or calculated.

In the compression set test, cured samples were compressed 25% for 1 day at 70°C., and the deformation after removal of the load was measured.

In sample (i), protein was not removed from the rubber; in sample (ii), protein was removed from the rubber, but using a soap of a sparingly soluble carboxylic acid (potassium laurate), and a sparingly soluble carboxylic acid (lauric acid) was added during compounding; in sample (iii), the protein was removed from the rubber according to this invention, and a rubber-soluble carboxylic acid (in the form of a zinc salt) was added during compounding. The improved proper-

ties of sample (iii) in comparison with samples (i) and (ii) are manifest.

Example 2.

To portions of preserved latex having a pH of 10 and a DRC of approximately 60% by weight were added the potassium salts of various fatty acids, including several naphthenic acids of different acid numbers, at a concentration of 1% on DRC, calculated as the free acids. The enzyme (subtilisin) was then added at a concentration of 250 ppm (on DRC) of active enzyme. For control purposes, to one portion of latex neither potassium salt nor enzyme was added; to another portion 1% by weight of a naphthenic acid as its potassium salt was added, but no enzyme and to another portion enzyme was added, but no potassium salt. The various combinations of fatty acids and enzyme are given in Table

- III. The mixtures were then incubated for 24 hours at about 35° C. After incubation the mixtures were each diluted to a low solids content (3% by weight total solids) before coagulation with acid in the normal way. After coagulation the coagula were creped and dried in warm air in the usual way. Analysis figures for the dried coagula are given in Table III.

TABLE III

Fatty acid	Enzyme	Protein (% by weight DRC)
None	None	1.06
None	250 ppm	0.63
Versatic (Registered Trade Mark)	250 ppm	0.38
2-Ethylhexanoic	250 ppm	0.56
Naphthenic 230	250 ppm	0.25
Naphthenic 180	250 ppm	0.25
Naphthenic 120	250 ppm	0.50
Naphthenic 230	None	1.06

- The potassium salts of naphthenic 230 and naphthenic 180, in combination with the enzyme, gave coagula with low protein contents (0.25% by weight). The potassium salts of Versatic, 2-ethylhexanoic and naphthenic 120 in combination with the enzyme gave coagula with higher protein contents and were therefore somewhat less efficient in preventing thickening due to particle association.

Example 3.

- Enzyme deproteinised natural rubber prepared by the method of Example 1 (experimental rubber 3 of Table I) was compounded

and vulcanized in the usual way according to the formulation shown in Table IV below. For comparative purposes a normal non-deproteinised grade of natural rubber SMR5CV, which contained about 2.5% by weight protein, was also compounded and vulcanized in (a) a similar formulation to the one used for the deproteinised rubber and (b) one differing only in the replacement of zinc 2-ethylhexanoate by stearic acid. The time and temperature of vulcanization for all three vulcanizates was 90 minutes at 140° C. The physical properties of the three vulcanizates are given in Table IV.

TABLE IV

Parts by weight

	Enzyme deproteinised rubber	SMR5 CV (a)	SMR5 CV (b)
Rubber	100	100	100
Zinc oxide	5	5	5
SRF Black N770	25	25	25
Zinc 2-ethylhexanoate	2	2	—
Stearic acid	—	—	2
Antioxidant	2	2	2
Sulphur	0.6	0.6	0.6
N-morpholinylbenzthia- zole-2-sulphenamide	1.44	1.44	1.44
Tetrabutylthiuram disulphide	0.6	0.6	0.6
Properties			
Hardness, IRHD	48	48	51
Tensile strength, MNm ⁻²	28	26	26
Elongation at break, %	600	590	570
Compression set, %	6	9	13
Resilience at 50°C, %	94	89	86
Stress relaxation rate, % per decade	1.8	2.3	3.0

5 In the stress relaxation test, the samples were stretched by 100% at room temperature and the tension noted at intervals of time up to approximately 1000 minutes. The rate of stress relaxation was obtained from a graph of tension plotted against the logarithm of time. In the compression set test, samples were compressed 25% for 1 day at 70°C, and the deformation after removal of the load was measured.

10 The resiliences were measured with a Dunlop tripmeter machine.

15 Properties progressively improved by replacing stearic acid with zinc-2-ethylhexanoate and SMR5CV by enzyme deproteinised rubber. In particular, compression set and stress

relaxation rate are reduced and resilience is increased.

Our co-pending British application no. 7513/1971 (Serial No. 1,360,852) relates to a vulcanized natural or synthetic rubber, in which:—

a) one of the non-rubber ingredients is from 0.5 to 5 pphr of a zinc, cadmium or lead salt of one or more saturated branched-chain aliphatic or alicyclic carboxylic acids, and

b) each of the non-rubber ingredients present is either completely insoluble in the rubber, or, if soluble, is present in the vulcanized rubber in a smaller concentration than that which would provide a saturated solution therein.

WHAT WE CLAIM IS:—

1. A method of removing protein from natural rubber, which method comprises incubating natural rubber latex with a proteolytic enzyme at a pH suitable for the enzyme in the presence of a soap to prevent premature thickening or coagulation of the latex and subsequently separating proteinaceous material from the rubber, wherein the acid constituent of the soap is one or more carboxylic acids which form rubber-soluble zinc salts.

2. A method as claimed in claim 1, wherein the natural rubber latex is incubated with from 10 to 1000 ppm of active enzyme by weight on the weight of the dry natural rubber for from 12 to 60 hours at from 40° C to 25° C.

3. A method as claimed in claim 1 or claim 2, wherein subtilisin or alkaline protease is used as the enzyme at a pH of from 9.5 to 11.

4. A method as claimed in any one of claims 1 to 3, wherein the proportion of the soap is from 0.1% to 10% by weight on the weight of the dry natural rubber content of the latex.

5. A method as claimed in any one of claims 1 to 4, wherein the acid constituent of the soap is one or more branched chain aliphatic or alicyclic carboxylic acids which form rubber-soluble zinc salts.

6. A method as claimed in claim 5, wherein the acid constituent of the soap is a grade of naphthenic acid.

7. A method as claimed in claim 5 or claim 6, wherein the acid constituent of the soap includes an alkyl chain at least 6 carbon atoms long.

8. A method as claimed in any one of claims 1 to 7, wherein proteinaceous material is separated from the rubber by coagulating the rubber latex at a solids content of from 1% to 30% by weight.

9. A method as claimed in any one of claims 1 to 7, wherein proteinaceous material is removed from rubber by centrifuging the latex.

10. A method as claimed in any one of

claims 1 to 9, and substantially as hereinbefore described in either of Examples 1 and 2.

11. Natural rubber from which protein has been removed by the method claimed in any one of claims 1 to 10.

12. Natural rubber as hereinbefore defined, containing:—

(i) not more than 1% by weight of proteinaceous material based on the weight of natural rubber alone; and

(ii) one or more added carboxylic acids, or salts thereof, which acids form rubber-soluble zinc salts.

13. Natural rubber as claimed in claim 12, wherein there is present not more than 0.5% by weight of proteinaceous material based on the weight of natural rubber alone.

14. Vulcanized natural rubber prepared from the natural rubber claimed in claim 12 or claim 13, in which:—

(a) there is present not more than 1% by weight of proteinaceous material based on the weight of natural rubber alone; and

(b) there is present a zinc, cadmium or lead salt of a carboxylic acid; and

(c) each non-rubber ingredient being either completely insoluble in the rubber, or, if soluble, being present in the vulcanized rubber in a smaller concentration than that which would provide a saturated solution therein.

15. Vulcanized natural rubber as claimed in claim 14, wherein there is present not more than 0.5% by weight of proteinaceous material based on the weight of natural rubber alone.

16. Vulcanized natural rubber as claimed in claim 14 or claim 15, wherein there is present from 0.5% to 10% by weight of a zinc salt of a carboxylic acid in solution in the vulcanized rubber.

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