

PATENT SPECIFICATION

(11) 1 255 645

NO DRAWINGS

- (21) Application No. 43528/68 (22) Filed 12 Sept. 1968
 (23) Complete Specification filed 11 Sept. 1969
 (45) Complete Specification published 1 Dec. 1971
 (51) International Classification C 08 c 1/00, 5/00; C 08 d 5/02
 (52) Index at acceptance

C3E 2BX

C3P 2B3D 2B3E1 2B3EX 2D1A2 2D1B2 2D2A2 2D8B
2K7 2K8 2RX

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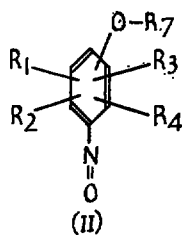
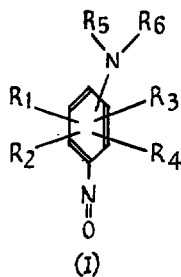


(54) TREATMENT OF RUBBER LATEX

(71) We, THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, a British Company, of 19 Buckingham Street, Adelphi, London, W.C.2., 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 the treatment of rubber latex with a view to modifying the properties of rubber prepared therefrom, and particularly, though not exclusively, with a view to providing the rubber with a rubber-bound antioxidant which cannot be leached out. The invention provides a process for the treatment of rubber latex, which process comprises mixing a latex of natural rubber or of a synthetic rubber having an unsaturated carbon chain with a nitrosophenol or nitrosoaniline and effecting reaction between the rubber and the nitroso compound so as to provide aminophenol groups or phenylenediamine groups chemically bound to the rubber molecules.

The aromatic nitroso compound may preferably have the formula:—

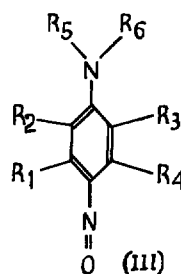


where R_1 , R_2 , R_3 and R_4 may be the same or different and each represent a hydrogen atom, a functional group, or a saturated or unsaturated hydrocarbon group which may be substituted by a functional group, or may in the case of formula (I) form one or more additional aromatic rings fused to the aromatic

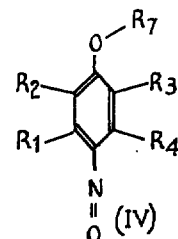
ring shown in the formula, provided that said groups or aromatic rings are not so large and so positioned as to prevent the functional — NR_5R_6 or — OR_7 group from exerting its antidegradant effect or the reaction of the nitroso compound with the rubbery polymer;

R_5 , R_6 and R_7 may be the same or different and each represent a hydrogen atom, or a saturated or unsaturated hydrocarbon group which may be substituted by a functional group, or R_5 and R_6 together with the nitrogen atom to which they are attached form a heterocyclic ring which may contain one or more other hetero atoms.

Preferred aromatic compounds which may be used in the process of this invention are those which contain the — NR_5R_6 or OR_7 group in a position *para* to the nitroso group. Such preferred compounds have the following general formulae:—



or



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 have the same meaning as defined above.

Examples of specific aromatic nitroso compounds which are preferred for use according to the present invention are as follows:—

N,N-dimethyl-p-nitrosoaniline
 N,N-diethyl-p-nitrosoaniline
 p-nitrosodiphenylamine
 p-nitrosophenol
 2-methyl-4-nitrosophenol

3-methyl-4-nitrosophenol
N-methyl-p-nitrosoanthranilic acid
N-p-nitrosophenyl-2-aminopropionic acid
N-(p-nitrosophenyl)-diethanolamine

5 The preferred aromatic nitroso compounds are the para-nitrosoanilines which may have additional functional groups, e.g., carboxylic acid or hydroxyl groups, either attached to the aromatic ring or incorporated in one or both of the groups attached to the amine nitrogen atom.

10 The process of the invention can be used to treat latices of both natural and synthetic rubbery polymers containing unsaturated carbon-carbon linkages, or other groups capable of suitable reaction with the compounds of formulae I, II, III and IV above. Rubbery polymers normally regarded as saturated polymers, which contain very low amounts of unsaturation for vulcanization purposes, for example, ethylenepropylene terpolymers and butyl rubber, are not suitable for treatment.

20 Examples of synthetic rubbers which have been successfully treated in latex form are cis - polyisoprene, styrene - butadiene copolymers, acrylonitrile - isoprene copolymers, carboxylated butadiene acrylonitrile polymers, and polychloroprene.

30 Natural rubber latex to be treated may be in the form of field latex or of a diluted or concentrated latex. The latex may have been preserved in any desired manner. It may be advantageous to treat the natural rubber latex before it has been stored for any substantial length of time.

35 The aromatic nitroso compound may conveniently be added to the rubber latex in the form of an aqueous ball-milled dispersion or as a solution in any suitable solvent. The proportion by weight of the aromatic nitroso compound added to the latex depends on the purpose for which it will be required, but will generally be within the range of 0.1 to 20 pphr. Nitrosoamines used for their antioxidant effect are preferably added in an amount of from 0.1 to 3.0 pphr, particularly from 0.2 to 1.0 pphr. Larger proportions of nitrosophenols, for example, from 1 to 5 pphr, may be required if comparable antioxidant effects are to be obtained. Nitroso compounds containing active groups intended to modify the properties of the rubber may be added to the latex in amounts of from 1.0 to 20 or even more pphr, depending upon the degree of modification desired.

55 After addition, the aromatic nitroso compound may, according to one aspect of the invention, be reacted (or allowed to react) with the rubber latex before coagulation of the latex. The time required for reaction depends on the temperature, but we have found that reaction is substantially complete in field or concentrated natural rubber latex after 10 days at ambient temperature of 20 to 35°C. In cases where the latex is heated, we prefer to avoid

temperatures above about 50°C, because higher temperatures tend to cause darkening and premature coagulation.

65 It is particularly advantageous to allow the aromatic nitroso compound to react with natural rubber latex at ambient temperatures. Treatment of natural rubber latex in this way can have several important advantages, since during export from the producing to consuming countries the concentrated latex undergoes long periods of storage which can be used to effect the reaction.

70 The presence of an efficient rubber-bound antioxidant may make further addition of antioxidants unnecessary. In the production of raw rubber from fresh latex the incorporation of a rubber-bound antioxidant may increase stabilization against oxidative deterioration during storage or processing.

80 According to another aspect of the invention, the rubber latex may be coagulated (either naturally or by acid or by any other desired method) before any or all of the reaction with the aromatic nitroso compound has taken place. The reaction may be effected, in this case, during storage of the wet coagulum at ambient temperatures, during normal drying of the raw rubber, or during compounding of the dry rubber, before vulcanization. The reaction may conveniently be effected by heating the treated coagulated latex at a temperature of from 50°C to 250°C, particularly 100°C to 200°C for from 60 to 0.5 minutes, higher temperatures requiring shorter reaction times. An advantage of this process is that it is in any case usual to heat the coagulum in order to dry it; convenient combined drying and reaction conditions are provided by heating the wet coagulum at from 80°C to 130°C or from 24 to 4 hours. Another advantage is that it enables well-protected rubbers of low viscosity to be prepared.

105 Generally, the treated rubber which has reacted with the nitroso compound will be compounded with such fillers, additives, vulcanizing agents and other compound ingredients as may be desired for the final vulcanized or unvulcanized rubber composition. The treatment of the invention is equally suitable for the production of filled and gum vulcanizates. When reaction between the rubber and the nitroso compound has taken place in the latex, then the rubber may be compounded either as a latex or after coagulation. Rubber latex is sometimes used without vulcanization, and the treated latex of this invention is suitable for such use. The treated rubber may be compounded using any desired technique.

120 Further processing of the latex, which may be effected, before, during, or after reaction with the aromatic nitroso compound, may be by any convenient method, for example, air-drying, coagulation, dipping or foaming.

125 The invention also includes a mixture of rubber latex with the aromatic nitroso com-

pound hereinbefore defined, before, during or after reaction between the two. Also included are raw and vulcanized rubbers whose resistance to degradation has been improved, or whose properties have been modified, by an aromatic nitroso compound by the various aspects of the process hereinbefore described.

The following Examples illustrate the invention. In the Examples, the compound *p*-nitrosodiphenylamine, which is the preferred compound for rubber-bound antioxidants, is referred to as NDPA. Parts are by weight per 100 parts of dry rubber (pphr).

EXAMPLE 1

Rate of reaction of NDPA with NR latex at room temperature

Two latex concentrates, low ammonia (LA) and high ammonia (HA), were used, and two levels of NDPA tested. The latices were mixed with amounts of a 50% aqueous ball-milled dispersion of NDPA required to give 0.3 or 0.5 parts of NDPA per 100 parts of dry rubber. They were then stored in glass flasks at room temperature, 1g samples taken at 0, 3, 6 and 10 days and poured into 50 mls. of acetone, and the coagulum allowed to soak in the solvent for 24 hours at room temperature. The concentration of NDPA in the acetone was measured colorimetrically via the red palladium chloride complex at 422 mμ. The results are shown in Table 1.

TABLE 1

Recovery of NDPA from NR latex

No.	Latex type	NDPA level	% recovery of NDPA after days at room temp.			
			0	3	6	10
1	LA	0.3	89	45	14	0
2	LA	0.5	94	64	*	0
3	HA	0.3	95	54	*	0
4	HA	0.5	93	67	25	0

* not measured.

These results show clearly that the reaction is completed in 7 to 10 days at room temperature (ca 20°C). It has been found that reaction occurs rather faster between NDPA and fresh field latex, the reaction being nearly complete after 3 days.

EXAMPLE 2

Preparation of dry rubbers from treated latex

For subsequent testing rubbers were prepared from latices 1—4 described above, and from four other latices. These were as follows:—

Latex	Type	Additive	Level
5	HA	None	—
6	HA	NDPA	0.3
7	HA	NDPA	0.5
8	HA	DBNPD*	0.5

* N,N-di-β-naphthyl-p-phenylenediamine, Ageite White.

Latices 6—8 were coagulated as described below immediately after mixing with the additive, i.e., without the 10 day maturing of

latices 1—4. The rubbers were prepared to simulate the commercial Heveacrub process as follows:—

The latex was diluted with an equal volume of water and treated with castor oil (0.7 pphr) with stirring, and coagulated by pouring into aqueous acetic acid (2%). The coagulum was crumbled within 2 hours of washing on a laboratory crepeing mill, and the rubber dried in an air oven at 100°C for 2 hours, followed by 4 hours at 55°C. These drying conditions were sufficient to effect reaction between the rubber and the NDPA.

Ageing resistance of raw rubbers from treated latex

The ageing resistance or oxidizability of raw rubber is determined by measuring its Plasticity Retention Index (PRI) before and after an extraction stage involving extraction with cold methanol/acetone/chloroform azeotrope for 72 hours followed by drying at 10⁻² mm mercury for 24 hours. This involves the measurement of the plasticity of the rubber before and after heat ageing for 30 minutes at 140°C, the percentage retention of the origi-

nal value giving the PRI, which can be related to the performance of the rubber after vulcanization. High PRI values are considered desirable, although for some applications low initial plasticities are required. Although the property measured in this test is viscosity, the term "plasticity" is used to emphasize that the PRI test relates to a particular instrument (the Wallace Plastimeter) and to a particular set of ageing conditions.

The results of plasticity measurements on the rubber samples prepared from latices 1—8 de-

scribed above are shown in Table 2 together with Mooney viscosities. The control rubber (5) has an initial plasticity of 67, which is of the order expected for a rubber prepared from preserved latex, and, similarly, a low PRI showing little resistance to ageing. The commercial antioxidant (8) gives little change in the initial plasticity, but imparts considerable resistance to ageing. The initial plasticities of the NDPA matured LA latices are a little lower than the control, whereas those of the HA latices are somewhat higher.

TABLE 2

Plasticity and PRI of raw rubbers

Rubber	Additive	Level	Initial Plasticity	PRI before extraction	PRI after extraction	Mooney viscosity ML (1+4 mins/100°C)
1	NDPA	0.3	61	50	73	110
2	NDPA	0.5	56	51	66	106
3	NDPA	0.3	74	64	82	122
4	NDPA	0.5	74	66	81	122
5	None	—	67	21	3	100
6	NDPA	0.3	36	59	62	73
7	NDPA	0.5	27	50	60	59
8	DBNPD	0.5	70	72	5	99

In all cases the PRI values before extraction are substantially improved over that of the control rubber 5. In all cases, the PRI values after extraction are substantially improved over those of the control rubbers 5 and 8 and demonstrate clearly that rubber-bound antioxidant groups have been incorporated.

The rubbers prepared immediately after addition of the NDPA (6, 7) show the peptizing or degrading effect observed in dry rubber mixing when the rubber and nitroso compound are heated together in air, the initial plasticities being considerably lower than those of the control or 'matured' rubbers. The PRI values are, however, of the same order, and this combination may be useful in the preparation of rubbers of low but constant plasticity.

The Mooney viscosities confirm the trend of the initial plasticities, although the 'matured' rubbers give somewhat higher values than the control.

EXAMPLE 3

Vulcanizates were prepared as follows.

1 to 4. Latices were treated as described in

Example 1, allowed to stand at ambient temperature for 10 days, then diluted with an equal volume of water, treated with castor oil (0.7% on the dry rubber) with stirring, and coagulated by pouring into aqueous acetic acid (2%). The coagulum was washed and creped and the rubber dried in an air oven at 100°C for 2 hours followed by 4 hours at 55°C. The vulcanizates were based on the formulation:—

Rubber	100	
Zinc oxide	5	60
Stearic acid	2	
CBS	0.5	
Sulphur	2.5	
Cure time	40/140°C.	

5 to 8. Latices were treated (Nos. 6—8) and immediately coagulated as described in Example 2. The vulcanizates were based on the formulation given above for vulcanizates 1 to 4.



Oxidative ageing of treated dry rubbers

The rates of oxidation of vulcanizates prepared as described above were measured before and after extraction with the methanol/acetone/chloroform azeotrope. Sheets 0.3 mm thick were prepared by vulcanization as indicated above. The oxygen absorption in pure oxygen at 100°C was measured on 10 cm × 0.5 cm strips before and after an extraction process consisting of cold extraction for 24 hours under nitrogen with methanol/acetone/

chloroform azeotrope in a Soxhlet apparatus, followed by a similar hot extraction, the solvent being removed from the extracted strips by pumping at 10⁻² mm of mercury for 24 hours.

Table 3 shows the time (T₁) in hours required for the specimens to absorb 1% w/w of oxygen, calculated on the total weight of vulcanizate. The results show that all the NDPA treated vulcanizates contain an effective antioxidant before extraction, and that this activity is largely retained after extraction.

TABLE 3

Oxidation of vulcanizates of treated rubber

Rubber	Additive	Level	Hours to 1% absorption	
			Unextracted	Extracted
1	NDPA	0.3	20.8	9.3
2	NDPA	0.5	25.2	16.0
3	NDPA	0.3	30.3	7.7
4	NDPA	0.5	35.4	11.0
5	None	—	8.6	1.5
6	NDPA	0.3	33.6	7.4
7	NDPA	0.5	50.0	7.9
8	DBNPD	0.5	30.5	2.6

Technological ageing of vulcanizates from treated rubbers.

25

Samples of the vulcanizates described above

were subjected to air oven ageing at 100°C before and after azeotrope extraction. The results are summarized in Table 4.

TABLE 4

Air oven ageing of vulcanizates prepared from modified dry rubbers

Rubber	Unextracted Unaged			Unextracted Aged 2 days/100°C			Extracted Aged 1 day/100°C		
	TS	EB	M300%	TS	EB	M300%	TS	EB	M300%
1	274	725	21	18	315	17	153	590	24
2	273	705	24	32	370	22	222	595	30
3	276	730	21	127	560	21	220	625	25.5
4	267	705	22	183	575	28.5	253	635	28.5
5	278	775	16.5	6	135	—	6	245	—
6	294	725	21	148	580	22	236	630	27
7	226	680	23	—	—	—	273	640	29
8	270	750	17.5	20	370	15	14	320	12

TS = tensile strength (kg/cm²)

EB = elongation at break (%)

M300% = modulus 300% (kg/cm²)

The results show that the rubbers obtained have initial properties equivalent to those of the controls, with the exception of 7 which was known from results given above to be badly peptized. The unextracted ageing results confirm the presence of the antioxidants, while the ageing after extraction demonstrates clearly that it is bound to the rubber, the protection increasing with increasing amount of NDPA used.

EXAMPLE 4

Vulcanizates were prepared as follows.

1 to 4. Latices were treated as described in Example 1 and allowed to stand at ambient temperature for 10 days. Air dried films were prepared by compounding the treated latices with 1 pphr each of zinc oxide, sulphur and

zinc diethyldithiocarbamate and vulcanized by heating in air for 30 minutes at 100°C.

8 was a control, formed by compounding an untreated latex with the compounding ingredients used for rubbers 1 to 4 except that 0.5 pphr of DBNPD was also added, and vulcanizing an air dried film of the compounded rubber for 30 minutes at 100°C.

Oxidation of latex vulcanizates.

Samples of the latex film vulcanizates were oxidized at 100°C in pure oxygen at 1 atmosphere before and after azeotrope extraction, and also after boiling for 1 hour with a 2% aqueous solution of a commercial detergent. The times for the absorption of 1% w/w of oxygen are shown in Table 5.

TABLE 5

Oxidation of latex vulcanizates at 100°C

Rubber	Hours to 1% absorption		
	Unextracted	Azeotrope	Detergent
1	85	27	32
2	60	32	34
3	103	41	26
4	94	47	33
8	118	7	10

The results again show that a rubber-bound antioxidant is present in the NDPA-treated vulcanizates, and that they have superior oxidation resistance to the conventionally protected vulcanizate after both treatments.

Samples of the above vulcanizates were subjected to air oven ageing at 100°C before and after azeotrope extraction. The results are summarized in Table 6.

TABLE 6

Ageing of vulcanizates of treated latex

Vulcanizate	TS	Unextracted Unaged		TS	Unextracted Aged 2 days/100°C		TS	Extracted Aged 2 days/100°C	
		EB	M ₅₀₀		EB	M ₅₀₀		EB	M ₅₀₀
1	303	810	40	202	665	57	110	820	20
2	339	805	50	205	610	85	135	745	33
3	342	855	37	241	735	43	125	815	22
4	349	825	45	228	690	55	180	790	36
8	345	830	36	235	735	37	3	520	3

Table 6 shows that before extraction the antioxidant action of the rubber-bound antioxidant is comparable with that of the conventional antioxidant. The trend is for the LA latex to be slightly less well protected against loss of tensile strength than the HA latex. On the other hand, the protection given by the conventional antioxidant after extraction and ageing is completely lost, whereas all the NDPA treated latices have given vulcanizates containing rubber-bound antioxidants.

All dried films having good antioxidant properties have also been prepared using a room temperature vulcanizing system such that the rubber was at no stage heated after admixture with the nitroso compound.

On the other hand, good results were obtained when the treated latex was heated to 70° for 16 hours to effect reaction between the rubber and the nitroso compound before compounding.

The coagulation and washing techniques described in Examples 1 to 4 are not critical. Similar results were obtained using other coagulating agents, e.g., orthophosphoric acid and other washing procedures. Similar results were also obtained when the preserved latex concentrate of Examples 1 to 4 was replaced by whole field latex.

EXAMPLE 5

Experiments were performed to observe the effect of adding NDPA to field latex under five different systems of processing. The five systems studied were:—

- immediate acid coagulation and processing into dry rubber.
- acid coagulation followed by a 10—12 day maturation period at ca. 20°C before processing into dry rubber.
- natural coagulation and processing into dry rubber.
- natural coagulation followed by a 10—12 day maturation period at ca. 29°C before processing into dry rubber.
- latex reaction for a 10—12 day period at ca. 29° before acid coagulation and processing into dry rubber.

For each system studied, a control rubber was prepared in addition to one with ca. 0.5% NDPA based on dry rubber content. All rubbers were dried at 52°—60°C in an air-circulating oven for ca. 16—20 hours.

The latex used was divided into ten lots of 200 gm dry rubber and half of them treated with ca. 0.5% NDPA on drc as a 33½ aqueous ball-milled dispersion. For system E, the latex was stabilized with ca. 0.7% ammonia based on latex. Azeotrope extraction was for 7 hours.

Properties of the dry rubbers are given in Table 7.

TABLE 7

Properties of raw modified rubbers and controls

System	Type of rubber	Before azeotrope extraction			After azeotrope extraction		
		N ₂ % wt.	Initial plasticity	PRI	N ₂ % wt.	Initial plasticity	PRI
A (acid coagulation)	Control	0.41	48	110	0.44	59	31
	Treated	0.50	52	61	0.51	55	71
B (acid coagulation matured 10 days)	Control	0.31	73	60	0.34	76	4
	Treated	0.43	64	64	0.42	68.5	74
C (natural coagulation)	Control	0.41	62	93	0.41	65	*
	Treated	0.46	77	79	0.44	82	80
D (natural coagulation matured 10 days)	Control	0.34	74	51	0.30	73	5
	Treated	0.40	70	70	0.36	80	69
E (latex reaction)	Control	0.49	65	78	0.49	60	*
	Treated	0.54	72	62	0.51	72	80

* plasticity too low to be measured.

The results show that the reaction of NDPA was successfully carried out with NR field latex as evidenced by:—

5 (i) increased nitrogen contents of the NDPA rubbers

(ii) improved oxidation resistance of the raw NDPA rubbers; after solvent extraction in each case.

10 As opposed to the NDPA reaction with concentrated latex, the addition of NDPA to field latex followed by immediate acid coagulation, crepeing and drying did *not* reduce the Wallace Plasticity of the NDPA rubbers. At 15 drying temperatures of 52—60°C, the NDPA rubbers were observed to be more cross-linked than their respective controls.

20 Gum and filled (tyre tread) vulcanizates prepared from rubbers B and E showed excellent technological properties and resistance to oxidation before and after azeotrope extraction particularly in the presence of copper ions.

EXAMPLE 6

Effect of NDPA modification on storage hardening

A major disadvantage of conventional natural rubbers is a process termed storage hardening which takes place between their preparation and use. It results in a considerable increase in Mooney viscosity and leads to greater power consumption in the processing machinery used. Currently certain new grades of NR are being produced as 'Constant Viscosity' rubbers by the addition of small amounts of a chemical to prevent this hardening reaction, which is associated with reactions of small amounts of aldehyde groups present in the rubber. It is possible for test purpose to accelerate the storage hardening by heating the rubbers at 60°C for 48 hours under vacuum over P₂O₅.

Fresh latex was treated with varying amounts of NDPA and converted to dry rubbers by the Heveacumb process. Each rubber was blended and the Mooney viscosities measured before and after accelerated storage hardening. The results are shown in Table 8.

TABLE 8

Storage hardening of NDPA modified rubbers

Sample Ref.	% wt. d.r.c.	Concentration of NDPA Mooney viscosity ML (1 + 4) at 100°C		
		Initial	After hardening	ΔV_R
CPS 9/1	Control	70	100½	30½
2	0.05	81	97½	16½
3	0.1	88	96	8
4	0.2	94	97	3
5	0.4	93	95	2

5 The results show clearly that the addition of as little as 0.1 pphr of NDPA almost completely prevents the occurrence of storage hardening.

EXAMPLE 7

Naturally coagulated rubbers with higher levels of NDPA

10 Bulk field latex was ammoniated to 0.04% w/w, and 3.5 kg batches treated with 0, 0.5, 1.0 and 2.0 pphr NDPA respectively, the order of addition of chemicals being 0.04% w/w sodium metabisulphite, 0.7% w/w cas-

tor oil, then the requisite amount of 33½% aqueous NDPA dispersion. They were allowed to stand at 20°C for 17 hours, by which time firm coagula had formed. Each coagulum was crumbed and dried at 100°C using a forced hot air draught for 4½ hours (3½ hours for the control).

Wallace Plasticities were measured before and after azeotrope extraction, and the results are shown together with nitrogen analyses on the extracted rubbers in Table 9.

TABLE 9

Raw rubber properties

% NDPA	Before azeotrope extraction		N % wt	After azeotrope extraction	
	Initial plasticity	PRI		Initial plasticity	PRI
Nil	56.5	85	0.42	59	44
0.5	63.5	89	0.44	66	80
1.0	58	78	0.51	60	85
2.0	22	77	0.61	23.5	85

30 The results show clearly the progressive reduction in plasticity with amounts of NDPA above 1 pphr due to the peptizing action of the nitroso compound described above. The method thus enables well-protected rubbers of low viscosity to be prepared.

EXAMPLE 8

Use of NDPA-modified latex in an unvulcanised composition

35 Unvulcanised compositions can be used as carpet backings, and NR latex is used for this purpose. A pre-reacted NDPA latex was prepared by treating NR latex with 0.25 or 0.5 pphr of NDPA and allowing it to stand at room temperature for 17 days.

It was then compounded as follows:—

Rubber (as latex)	100
Whiting	400
Dispersing agent	0.2
Non-ionic stabilizer	1
Thickener	0.3

and the composition hand spread at about 20 oz. per square yd. dry on rayon looped pile carpet. It was oven dried at 50°C for 30 minutes, and samples aged in an air oven at 70°C alongside similar materials prepared with unmodified latex. The time in days to produce cracking when the samples were flexed was noted, and the results are shown in Table 10.

They indicate that performance of the antioxidant modified rubber is at least equivalent to that of unmodified natural rubbers protected by conventional antioxidants.

TABLE 10

Ageing of unvulcanized carpet backing compositions at 70°C

Latex	Added antioxidant	Days to crack
NR	Antox*0.5 + TU**1	18
NR	Agerite AK***0.5 + TU 1	36
NR	None	5
NDPA 0.25	None	17
NDPA 0.25	TU 1	38
NDPA 0.5	None	36
NDPA 0.5	TU 1	38

* Antox = butyraldehyde-aniline condensation product.

** TU = thiourea.

*** Agerite AK = polymerized 2,2,4-trimethyl-1,2-dihydroquinoline.

EXAMPLE 9

Reaction of nitroso compounds with synthetic rubber latices

10 The reaction of NDPA with synthetic rubber latices was studied under two sets of conditions: —

15 (i) *Latex pre-reaction* — The NDPA was mixed with the latex and allowed to stand at 20°C, after which the latex was coagulated and the washed, creped rubber died either at room temperature or by heating in air.

(ii) *Reaction during drying* — The latex was coagulated within 1 hour of mixing in the

NDPA, the rubber washed and creped, and dried either at room temperature or by heating in air. 20

Raw rubber properties.

Evidence for the successful combination of the nitroso compound with the synthetic rubber was obtained from the effect on Wallace Plasticities after extraction with hot azeotrope and drying, and from the oxygen absorption figures after extraction, compared with control samples prepared without NDPA. The results are shown in Tables 11 and 12. 25 30

TABLE 11

Polymer	NDPA pphr	Pre-reaction time	Drying	Time to 1% O ₂ absorption of extracted rubbers at 125°C
Polychloroprene	1	14 days	room temp.	28
	1	0	5 hrs/90°C	35
	0	—	room temp.	16
Styrene-butadiene copolymer	1	0	5 hrs/90°C	>30
	0	—	5 hrs/90°C	1
Carboxylated butadiene acrylonitrile copolymer	1	20 days	room temp.	>40
	0	—	room temp.	4

(16)

TABLE 12

Polymer	NDPA pphr	Pre-reaction time	Drying	Initial plasticity	PRI after extraction
Cis-polyisoprene	1	14 days	room temp.	49	73
	1	14 days	4 hrs/90°C	46	59
	1	0	4 hrs/90°C	14	53
	0	—	room temp.	28	25 — unextracted
	0	—	4 hrs/90°C	liquefies during heating	
Isoprene-acrylonitrile	1	10 days	room temp.	33	73
copolymer	0	—	room temp.	27	19

Reaction of functionally substituted nitroso compounds with NR latex concentrate.

5 The reaction of nitroso compounds with latex provides a simple route to the introduction into the rubber molecule of functional groups which the nitroso compound contains. Thus beneficial effects may be obtained from the introduction of e.g., carboxylic acid, 10 hydroxyl, and other groups which as well as modifying the essentially non-polar nature of the rubber could serve as the site for further chemical reactions such as cross-linking. Three such compounds are given in Examples 10 to 15 12.

EXAMPLE 10

20 *N* - methyl - *p* - nitrosoanthranilic acid was added to latex in an amount corresponding to 4 pphr. In one case the latex was allowed to stand for 12 days at 28—30°C before the rubber was coagulated with a water/alcohol mixture containing 1% acetic acid, creped, and dried at room temperature. In a second 25 experiment the latex was coagulated by acid within 1 hour of the addition, the coagulum allowed to stand at 28—30°C for 14 days, the rubber creped and dried at room temperature. PRI and nitrogen analyses after extraction confirmed the presence of a rubber-bound oxidant.

EXAMPLE 11

30 *N* - *p* - nitrosophenyl - 2 - aminopropionic acid was reacted with a natural rubber latex concentrate in the manner described for the anthranilic acid above for 12 days at 22°C. 35 The latex was then coagulated with 1% acetic acid solution, creped and dried at room temperature. In another experiment the latex was coagulated in 1% acetic acid solution within 1 hour of the addition. The coagulated rubber 40 was then creped and dried at 100°C for 5 hours. In both experiments, reaction between the rubber and the nitroso compound occurred.

EXAMPLE 12

N - (*p* - nitrosophenyl - diethanolamine was added to natural rubber latex at a level of 5 45 pphr and the latex allowed to stand at 22°C for 12 days). The latex was then coagulated with 1% acetic acid solution, creped and dried at room temperature. In a second experiment 50 5 pphr of the compound was added to the latex which was coagulated within 1 hour of the addition, creped and dried for 5 hours at 100°C. In both cases, reaction took place between the rubber and the nitroso compound.

Modification of natural rubber latex concentrate with p - nitrosophenol.

EXAMPLE 13

Latex (257g) was treated with 5 pphr of dry *p*-nitrosophenol and 7.5 mls of 20% potassium laurate laurate solution, and allowed to stand 60 for 18 days at 25°C, about 5 mls of concentrated ammonia (d 0.880) being added during storage to maintain fluidity. A portion (110g) was coagulated with 1% acetic acid, creped and dried at room temperature for 3 days. 65

EXAMPLE 14

Two batches of latex were compounded as follows:—

Rubber (as latex)	100	100	
<i>p</i> -nitrosophenol (dry.)	5	2	70
50% zinc diethyl-dithiocarbamate	5	—	
Water	167	167	

Each mixture was stirred for 15 minutes 75 and then coagulated in 1.5% acetic acid, creped and dried for 5 hours at 100°C. The PRI values, before and after extraction, of the products of Examples

13 and 14 confirmed the formation of a rubber-bound antioxidant.

Patent Specn. No. 1185896 describes and claims a process for improving the resistance to degradation of an unsaturated natural or synthetic rubber, which process comprises reacting the rubber polymer, in the presence of the fillers, additives, vulcanizing agents and other compounding ingredients which are required for the final rubber composition, at least one filler, additive, vulcanizing agent or other compounding ingredient being present during the reaction, with an aromatic nitroso compound substantially as hereinbefore defined with reference to Formulae I and II. Optionally the rubbery polymer is used in the latex state, and the aromatic nitroso compound is added in the form of a solution or ball-milled dispersion in a suitable solvent before, after or together with solutions or ball-milled dispersions of

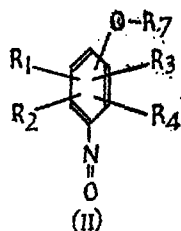
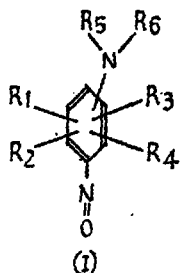
such fillers, pigments, anti-degradants, vulcanizing ingredients and other compounding ingredients as required in the final vulcanizate.

We make no claim to the process claimed in Patent Specn. No. 1185896. Subject to this disclaimer, we declare that

WHAT WE CLAIM IS:—

1. A process for the treatment of rubber latex, which process comprises mixing a latex of natural rubber or of a synthetic rubber having an unsaturated carbon chain with a nitroso-phenol or nitrosoaniline and effecting reaction between the rubber and the nitroso compound so as to provide aminophenol groups or phenylenediamine groups chemically bound to the rubber molecules.

2. A process as claimed in claim 1, wherein the aromatic nitroso compound has the formula:—



where R_1 , R_2 , R_3 and R_4 may be the same or different and each represent a hydrogen atom, a functional group, or a saturated or unsaturated hydrocarbon group which may be substituted by a functional group, or may, in the case of formula (I) form one or more additional aromatic rings fused to the aromatic ring shown in the formula, provided that said groups or aromatic rings are not so large and so positioned as to prevent the functional — NR_5R_6 or OR_7 group from exerting its anti-degradant effect or the reaction of the nitroso compound with the rubbery polymer;

R_5 , R_6 and R_7 may be the same or different and each represent a hydrogen atom or a saturated or unsaturated hydrocarbon group which may be substituted by a functional group, or R_5 and R_6 together with the nitrogen atom to which they are attached form a heterocyclic ring which may contain one or more hetero atoms.

3. A process as claimed in claim 2, wherein the aromatic nitroso compound is a p-nitrosoaniline.

4. A process as claimed in claim 3, wherein the aromatic nitroso compound is n-nitrosodiphenylamine.

5. A process as claimed in any one of claims 1 to 4, wherein the rubber latex is a natural rubber latex.

6. A process as claimed in any one of claims 1 to 4, wherein the rubber latex is a synthetic rubber latex.

7. A process as claimed in any one of claims 1 to 6, wherein the proportion by weight of the aromatic nitroso compound added is from 0.2 to 1.0% of the dry rubber content of the latex.

8. A process as claimed in any one of claims 1 to 7, wherein the aromatic nitroso compound is reacted (or allowed to react) with the rubber latex before coagulation of the latex.

9. A process as claimed in claim 8, wherein the aromatic nitroso compound is allowed to react with the rubber latex at ambient temperature.

10. A process as claimed in claim 8 or claim 9, wherein the treated rubber latex is compounded and processed to form the desired vulcanized or unvulcanized rubber composition.

11. A process as claimed in any one of claims 1 to 7, wherein the rubber latex is coagulated before any or all of the reaction with the aromatic nitroso compound has taken place.

12. A process as claimed in claim 11, wherein the aromatic nitroso compound is allowed to react with the rubber during storage of the wet coagulum at ambient temperature.

13. A process as claimed in claim 11, wherein the aromatic nitroso compound is reacted with the rubber during drying of the wet coagulum at a temperature of from 80°C to 130°C for from 24 to 4 hours.

13 and 14 confirmed the formation of a rubber-bound antioxidant.

Patent Specn. No. 1185896 describes and claims a process for improving the resistance to degradation of an unsaturated natural or synthetic rubber, which process comprises reacting the rubber polymer, in the presence of the fillers, additives, vulcanizing agents and other compounding ingredients which are required for the final rubber composition, at least one filler, additive, vulcanizing agent or other compounding ingredient being present during the reaction, with an aromatic nitroso compound substantially as hereinbefore defined with reference to Formulae I and II. Optionally the rubbery polymer is used in the latex state, and the aromatic nitroso compound is added in the form of a solution or ball-milled dispersion in a suitable solvent before, after or together with solutions or ball-milled dispersions of

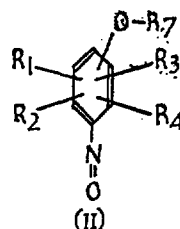
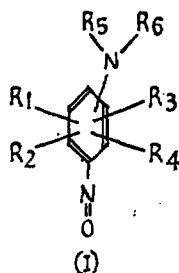
such fillers, pigments, anti-degradants, vulcanizing ingredients and other compounding ingredients as required in the final vulcanizate.

We make no claim to the process claimed in Patent Specn. No. 1185896. Subject to this disclaimer, we declare that

WHAT WE CLAIM IS:—

1. A process for the treatment of rubber latex, which process comprises mixing a latex of natural rubber or of a synthetic rubber having an unsaturated carbon chain with a nitroso-phenol or nitrosoaniline and effecting reaction between the rubber and the nitroso compound so as to provide aminophenol groups or phenylenediamine groups chemically bound to the rubber molecules.

2. A process as claimed in claim 1, wherein the aromatic nitroso compound has the formula:—



where R_1 , R_2 , R_3 and R_4 may be the same or different and each represent a hydrogen atom, a functional group, or a saturated or unsaturated hydrocarbon group which may be substituted by a functional group, or may, in the case of formula (I) form one or more additional aromatic rings fused to the aromatic ring shown in the formula, provided that said groups or aromatic rings are not so large and so positioned as to prevent the functional $—NR_5R_6$ or OR_7 group from exerting its anti-degradant effect or the reaction of the nitroso compound with the rubbery polymer;

R_5 , R_6 and R_7 may be the same or different and each represent a hydrogen atom or a saturated or unsaturated hydrocarbon group which may be substituted by a functional group, or R_5 and R_6 together with the nitrogen atom to which they are attached form a heterocyclic ring which may contain one or more hetero atoms.

3. A process as claimed in claim 2, wherein the aromatic compound is a p-nitrosoaniline.

4. A process as claimed in claim 3, wherein the aromatic nitroso compound is n-nitrosodiphenylamine.

5. A process as claimed in any one of claims 1 to 4, wherein the rubber latex is a natural rubber latex.

6. A process as claimed in any one of claims 1 to 4, wherein the rubber latex is a synthetic rubber latex.

7. A process as claimed in any one of claims 1 to 6, wherein the proportion by weight of the aromatic nitroso compound added is from 0.2 to 1.0% of the dry rubber content of the latex.

8. A process as claimed in any one of claims 1 to 7, wherein the aromatic nitroso compound is reacted (or allowed to react) with the rubber latex before coagulation of the latex.

9. A process as claimed in claim 8, wherein the aromatic nitroso compound is allowed to react with the rubber latex at ambient temperature.

10. A process as claimed in claim 8 or claim 9, wherein the treated rubber latex is compounded and processed to form the desired vulcanized or unvulcanized rubber composition.

11. A process as claimed in any one of claims 1 to 7, wherein the rubber latex is coagulated before any or all of the reaction with the aromatic nitroso compound has taken place.

12. A process as claimed in claim 11, wherein the aromatic nitroso compound is allowed to react with the rubber during storage of the wet coagulum at ambient temperature.

13. A process as claimed in claim 11, wherein the aromatic nitroso compound is reacted with the rubber during drying of the wet coagulum at a temperature of from 80°C to 130°C for from 24 to 4 hours.



14. A process as claimed in any one of claims 1 to 9, wherein the rubber latex is coagulated after completion of the reaction with the aromatic nitroso compound.
- 5 15. A process as claimed in any one of claims 11 to 14, wherein the coagulum is compounded and processed to form the desired rubber vulcanizate.
- 10 16. A process as claimed in claim 1 and substantially as hereinbefore described in any one of Examples 1 to 14.
17. A mixture of rubber latex with a nitroso-phenol or nitrosoaniline which is capable of reacting with the rubber to provide amino-phenol groups or phenylenediamine groups 15 chemically bound to the rubber molecules, before, during or after reaction between the two.
18. Rubber which has been treated by the process claimed in any one of claims 1 to 16.
19. A vulcanized or unvulcanized rubber 20 composition formed by the process claimed in claim 10 or claim 15.
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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.



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