GUIDANCE DOCUMENT

Natural Rubber within REACH

2006/1907/EC

Version 1

2 November 2008
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**Introduction**

This guidance document is the result of an investigation into the legal requirements associated with the importation of natural rubber (NR) within the framework of the Regulation 1907/2006/EC (REACH). The work was performed in cooperation with TARRC (Tun Abdul Razak Research Centre), RTAE (The Rubber Trade Association of Europe) and FECC (European Association of Chemical Distributors). The interpretation of the REACH requirements given by this guidance is based on an analysis of the legal text (REACH 2006) and the “Guidance for monomers and polymers” developed by the European Chemicals Agency (ECHA 2008).

After giving a brief overview of the REACH regulation on polymers and natural substances (Chapter 1), a general framework to assess the requirements associated with the importation of NR is presented (Chapter 2). The last two chapters are dedicated to applicable case studies elaborated for the most common grades of non-chemically-modified natural rubber (Chapter 3) and chemically-modified natural rubber (Chapter 4) available on the European market.

Given the high variety of forms in which NR is imported and placed on the market, it seemed necessary to develop specific guidance to support case-by-case evaluations. Even if this guidance document does not contain all natural rubber grades imported into EU, the methodology proposed and the case studies analysed represent a good basis for evaluating any other grades.

This guidance document may be revised in accordance with future needs and information.
1. Legislative background and existing guidance document

The following paragraphs give a general overview of the legal REACH framework on which the requirements related to the importation of NR are based. Paragraph 1.1 focuses on polymers and natural substances; Paragraph 1.2 on chemically-modified natural substances. The concepts introduced in this chapter are transferred to the decisional flow chart given in the next chapter.

1.1. Exemptions: polymers and natural substances

REACH exempts polymers from registration\(^1\), but the exemption is not extended to the monomer units for which registration is required. As explained in the ECHA’s guidance\(^2\) and as shown in Figure 1.1, polymers may include, beside the monomer units of which they are composed, impurities derived from the manufacturing process, additives to preserve the stability and additives to improve performance. Among these components, neither impurities nor additives to preserve stability require to be registered.

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\(^1\) REACH 2006. **Article 2(9):** “The provision of Title II [registration] and VI [evaluation] shall not apply to polymers”.

\(^2\) ECHA 2008. A polymer, as any other substance defined in Article 3(1), **can also contain additives necessary to preserve the stability of the polymer and impurities deriving from the manufacturing process.** These stabilisers and impurities are considered to be part of the substance and do not have to be registered separately. Stabilisers include, for example, heat stabilisers, anti-oxidants (both useful during extrusion) and light stabilisers (e.g. for preservation during use). Impurities are unintended constituents of the polymer such as catalyst residues or unreacted monomers.

**Substances may also be added to improve the performance of the polymer** even though they are not necessary for preserving the stability of the polymer. Indeed, substances are commonly added to a polymer for the purpose of adjusting or improving the appearance and/or the physico-chemical properties of the polymeric material. Examples of such substances include pigments, lubricants, thickeners, antistatic agents, antifogging agents, nucleating agents and flame retardants. When a polymeric material contains such substances it should be considered as a preparation or an article, as the case may be. **For such substances normal registration requirements apply**

Polymers are exempted from the provisions on registration of Title II of REACH (Article 2(9)). The manufacturer or importer of a polymer is therefore generally not required to provide to the Agency any information related to the intrinsic properties of the polymer itself, with the exception of its classification and labelling when applicable.
In addition, Article 2(7), by means of Annex V, exempts natural substances not chemically-modified that are below the criteria for classification as dangerous. In these circumstances, there is no requirement to identify the monomers or any other substances constituting the building blocks of the polymer.

![Diagram](Figure 1.1: What need to be registered in a synthetic polymer.)

1.2. Chemically modified natural polymers substances

If a natural polymer is chemically-modified, because, for instance, of post-treatment processes, registration of the monomers or any other substance which exceed 1 ton/year and represent 2% by weight or more of the polymer is required. Nevertheless, monomers and any other substance from which the natural polymer was derived can be considered as naturally-occurring and do not need to be registered.

In addition, for substances used for to modify the natural polymer, **registration is required only for those ending up chemically-bound with the polymer** in accordance with Art. 6(3) (≥ 1 ton/year and ≥ 2% w/w chemically-bound).

2. Assessment methodology and decisional flow-chart

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3 REACH 2006. Annex V: Exemptions from the obligation to register in accordance with Article 2(7)(b)

8. Substances which occur in nature other than those listed under paragraph 7, if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC or unless they are persistent, bioaccumulative and toxic or very persistent and very bioaccumulative in accordance with the criteria set out in Annex XIII or unless they were identified in accordance with Article 59(1) at least two years previously as substances giving rise to an equivalent level of concern as set out in Article 57(f).

[as amended by the Commission Regulation (EC) No 987/2008]
The considerations stated in the previous chapter, are here transferred to a decisional flow-chart to identify when a chemical should be registered. As the flow chart shows, the possible scenarios can be grouped into three:

- **No registration is required when:**
  - The criteria for classification as dangerous according to Directive 67/548/EEC are not fulfilled AND
  - No substances are added to natural rubber extracted from the tree; OR
  - Substances are added to maintain the stability of natural rubber but no chemical-modification occurs; OR
  - Substances are added to improve the performances of natural rubber, without chemical modification occurring, and their total quantity of each does not exceed 1 ton/year per importer; OR
  - Substances are added to chemically-modify natural rubber by less than 2% w/w.

- **Registration is required for added substances when:**
  - Substances are added to improve the performance of natural rubber and the presence of each exceeds 1 ton/year per importer.

- **Registration is required for monomers which have been chemically-bound to the natural rubber when:**
  - The chemical modification of natural rubber consists of at least 2% w/w and the total quantity of the chemically-bound monomer exceeds 1 ton/year per importer.
Extraction of Natural Rubber (including impurities derived from the coagulation process)

Addition of other substances

No other substances added

Addition of new substances

CHEMICAL MODIFICATION

NO CHEMICAL MODIFICATION

Physical/Chemical modification

PERFORMANCE IMPROVEMENT

STABILITY PRESERVATION

Stability/Performance purpose

≥2% w/w chemically-bound and ≥ 1 ton/year

> 1 ton/year

Criteria for registration

=YES  NO

YES  NO

Registration

REGISTER monomer units bound to the natural polymer

REGISTER substance(s) added to improve performance

NO REGISTRATION REQUIRED

THE MONOMER AND ANY OTHER SUBSTANCE FROM WHICH THE NATURAL POLYMER WAS DERIVED CAN BE CONSIDERED AS NATURALLY-OCCURRING AND DO NOT NEED TO BE REGISTERED (unless they meet the criteria for classification as dangerous in accordance to Directive 67/548/EEC and comply with the condition set in Annex V (8) (see footnote 3))
3. Case Studies 1: Natural Rubber – non-treated grades

3.1. TSR 10, TSR 20

![Diagram of the process]

<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical modification</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td>Yes/no</td>
<td>≥2%</td>
</tr>
<tr>
<td>Natural coagulation</td>
<td>-</td>
<td>-</td>
<td>NO</td>
<td>Coagulation</td>
</tr>
<tr>
<td>Processing</td>
<td>-</td>
<td>-</td>
<td>NO</td>
<td>Washing, crumbing, drying, baling</td>
</tr>
</tbody>
</table>

REACH implementation/actions:

- No registration required since no chemicals are added to the natural substance during any of the processes involved: coagulation, washing, crumbing, drying, baling.
### 3.2. TSR 3, 3L, 5, L, RSS (Ribbed Smoked Sheet), ADS (Air Dried Sheet)

![Diagram of latex processing]

<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical</th>
<th>Reason</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process</td>
<td>-</td>
<td>Chemical</td>
<td>Reason</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Concentration of impurities remaining in the final product:

- Ammonia: none remaining (neutralised by formic acid)
- Formic acid: < 0.001 % w/w

**REACH implementation/actions:**

Chemical modification of the original natural substance does not occur. Registration is not required since the only substances remaining, beside the natural rubber extracted from the tree, are impurities from the preservation/coagulation process which do not make the substance classifiable according to Directive 67/548/EEC.
3.3. Crepe Rubber types

<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical Reason</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ammonia</td>
<td>Prevent autocoagulation during transportation etc</td>
<td>Ammonia added to collected latex</td>
<td>Field latex</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Formic acid</td>
<td>Neutralise ammonia and coagulate latex</td>
<td>Formic acid added to latex</td>
<td>Coagulum</td>
</tr>
<tr>
<td>Processing</td>
<td>-</td>
<td>-</td>
<td>Milling, cutting, drying, pressing, baling</td>
<td>Crepe Rubber</td>
</tr>
</tbody>
</table>

Concentration of impurities remaining in the final product:

- Ammonia: none remaining (neutralised by formic acid)
- Formic acid: < 0,001 % w/w

REACH implementation/actions:

Chemical modification of the original natural substance does not occur. Registration is not required since the only substances remaining, besides the natural rubber extracted from trees, are impurities...
from the preservation/coagulation process which do not make the substance classifiable according to Directive 67/548/EEC.
4. Case studies 2: Natural Rubber – treated grades

This chapter contains several case studies of NR treated grades. The treatment is performed in order to prevent the process known as storage hardening, which, if it occurs, could compromise the subsequent processing of NR in manufacturing factories.

Storage hardening is characterised by increasing viscosity with time because of branching and crosslinking of chains through reaction of low levels of functional groups on the chains with some of the non-rubber species present in the rubber. Storage hardening can be prevented by blocking the functional groups with an added chemical, hydroxylamine neutral sulphate, in a process referred to as viscosity stabilisation. The grades of rubbers produced in this way are known as constant viscosity or CV rubbers.
4.1. **TSR CV (Constant Viscosity)**

- Latex from tree
  - Preserve with ammonia
- Field latex
  - Stabilise rubber viscosity
- Viscosity stabilised rubber latex
  - Coagulate with formic acid
- Coagulum
  - Process: wash, crumb, dry, bale
- TSR CV
<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical modification</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td>Yes/no</td>
<td>≥2%</td>
</tr>
<tr>
<td>Preserve</td>
<td>Ammonia</td>
<td>Prevent autocoagulation during transportation etc</td>
<td>NO</td>
<td>-</td>
</tr>
<tr>
<td>Stabilise rubber viscosity</td>
<td>Hydroxyl-amine neutral sulphate</td>
<td>Preserve the viscosity of the rubber</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Formic acid</td>
<td>Neutralise ammonia and coagulate latex</td>
<td>NO</td>
<td>-</td>
</tr>
<tr>
<td>Processing</td>
<td>-</td>
<td>-</td>
<td>NO</td>
<td>-</td>
</tr>
</tbody>
</table>

Concentration of impurities remaining in the final product:

- Hydroxyl-amine neutral sulphate: <0.03% w/w
- Ammonia: none remaining (neutralised by formic acid)
- Formic acid: <0.001% w/w

**REACH implementation/actions:**

As described at the beginning of this chapter, hydroxylamine neutral sulphate is used to stabilise the viscosity. Even if chemical modification of the original natural substance occurs, the amount of modification is very low, far below the 2% threshold required for registration of monomer units in the polymer.

Remaining concentrations of chemicals from the processes of viscosity preservation (hydroxylamine neutral sulphate) and coagulation (formic acid) do not compromise the classification of the substance, as for the case study 3.2.

Consequently, registration is not required for any of the chemicals involved.
4.2. TSR 10CV, 20CV (Constant Viscosity)

Latex from tree

- Natural coagulation

Cup lump

- Process: wash, crumb, dry

Dry ‘biscuit’

- Stabilise rubber viscosity

Viscosity stabilised rubber

- Bale

TSR 10CV, 20CV
<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical Reason</th>
<th>Yes/no</th>
<th>≥2%</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabilise rubber viscosity</td>
<td>Hydroxylamine neutral sulphate</td>
<td>Preserve the viscosity of the rubber</td>
<td>Yes</td>
<td>No</td>
<td>Hydroxylamine neutral sulphate added to dried rubber in extruder</td>
<td>Viscosity stabilised rubber</td>
</tr>
<tr>
<td>Bale</td>
<td>-</td>
<td>-</td>
<td>NO</td>
<td>-</td>
<td>Physical compaction</td>
<td>TSR 10 CV, 20 CV</td>
</tr>
</tbody>
</table>

Concentration of impurities remaining in the final product:

- Hydroxylamine neutral sulphate: <0.03 % w/w

**REACH implementation/actions:**

The only substance used during the process is hydroxylamine neutral sulphate. Registration is not required for the same reasons presented in case study 4.1.
4.3. SMR GP

Latex from tree

Natural coagulation

Cup lump

Field latex

Preserve with ammonia

Coagulate with formic acid

Coagulum

Process: wash, crumb

Crumb

Process: Wash, crumb

Crumb

Process: Blend, dry

Dry 'biscuit'

Process: Blend, dry

Stabilise rubber viscosity

Viscosity stabilised rubber

Bale

SMR GP
<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical</th>
<th>Reason</th>
<th>Yes/no</th>
<th>≥2%</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural coagulation</td>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td>Yes/no</td>
<td>≥2%</td>
<td></td>
<td>Coagulation</td>
</tr>
<tr>
<td>Preserve</td>
<td>Ammonia</td>
<td>Chemical</td>
<td>Prevent autocoagulation during transportation etc</td>
<td>No</td>
<td>-</td>
<td>Gaseous ammonia added to collected latex</td>
<td>Field latex</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Formic acid</td>
<td>Chemical</td>
<td>Neutralise ammonia and coagulate latex</td>
<td>No</td>
<td>-</td>
<td>Formic acid added to latex</td>
<td>Coagulum</td>
</tr>
<tr>
<td>Stabilise rubber viscosity</td>
<td>Hydroxylamine neutral sulphate</td>
<td>Chemical</td>
<td>Preserve the viscosity of the rubber</td>
<td>Yes</td>
<td>No</td>
<td>Hydroxylamine neutral sulphate added to dried rubber in extruder</td>
<td>Viscosity stabilised rubber</td>
</tr>
<tr>
<td>Processing</td>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td>Yes/no</td>
<td>≥2%</td>
<td></td>
<td>SMR GP</td>
</tr>
<tr>
<td>Bale</td>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td>Yes/no</td>
<td>≥2%</td>
<td></td>
<td>SMR GP</td>
</tr>
</tbody>
</table>

Concentration of impurities remaining in the final product:

- Ammonia: none remaining (neutralised by formic acid)
- Formic acid: <0.01% w/w
- Hydroxylamine neutral sulphate: <0.03% w/w

REACH implementation/actions:

Registration is not required for the same reasons presented in case study 4.1.
4.4. **Deproteinised Natural Rubber (DPNR)**

The protein in natural rubber contributes to creep in rubber products and is a major cause of swelling of rubber products in prolonged contact with water. In DPNR, unlike the previous case studies, these undesirable characteristics have to be minimised by reducing the protein content of the rubber through purification by digesting protein with a specific enzyme.
<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical</th>
<th>Reason</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td>Yes/no / ≥2%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preserve</td>
<td>Ammonia</td>
<td>Prevent</td>
<td>No</td>
<td>Gaseous</td>
<td>Field latex</td>
</tr>
<tr>
<td></td>
<td></td>
<td>auto coagulation during transportation etc</td>
<td></td>
<td>ammonia added to collected latex</td>
<td></td>
</tr>
<tr>
<td>Stabilise latex</td>
<td>Teric N10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Prevent</td>
<td>No</td>
<td>Non-ionic</td>
<td>Stabilised latex</td>
</tr>
<tr>
<td></td>
<td></td>
<td>coagulation during enzyme treatment</td>
<td></td>
<td>surfactant added to latex</td>
<td></td>
</tr>
<tr>
<td>Deproteinise</td>
<td>Protease enzyme protein</td>
<td>Digest</td>
<td>NO</td>
<td>Enzyme added</td>
<td>Low protein latex</td>
</tr>
<tr>
<td></td>
<td></td>
<td>protein in the latex</td>
<td></td>
<td>to the latex</td>
<td></td>
</tr>
<tr>
<td>Stabilise rubber viscosity</td>
<td>Hydroxyl-</td>
<td>Preserve</td>
<td>Yes</td>
<td>Hydroxyl-</td>
<td>Viscosity stabilised</td>
</tr>
<tr>
<td></td>
<td>amine neutral</td>
<td>the viscosity of the rubber</td>
<td>No</td>
<td>amine neutral sulphate</td>
<td>rubber</td>
</tr>
<tr>
<td></td>
<td>sulphate</td>
<td></td>
<td></td>
<td>sulphate added to latex</td>
<td></td>
</tr>
<tr>
<td>Coagulation with steam</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td>Washing,</td>
<td>DPNR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>crumbing, drying, baling</td>
<td></td>
</tr>
<tr>
<td>Processing</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remaining concentration of added chemicals:

- Ammonia: none remaining (neutralised by formic acid)
- Teric N10: < 0.1 % w/w
- Protease enzyme protein: < 0.01% w/w
- Hydroxylamine neutral sulphate: < 0.03 % w/w

**REACH implementation/actions:**

Registration is not required for any of the substances involved.

For hydroxylamine neutral sulphate see case study 4.1.

For teric N10<sup>4</sup>, registration is not required since it does not chemically modify the polymer and its function is to preserve stability. For protease enzyme protein, registration is not required since it does not chemically modify the natural polymer; it is used as part of the purification process. Moreover, in this case the concentration of the remaining chemicals does not compromise the classification of the substance.

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<sup>4</sup> Polyoxyethylene 10 phenol ether
4.5. MG Rubber (Methacrylate grafted rubber)

- 60% NR latex concentrate
  - Add emulsion of MMA and organic peroxide
  - MMA in NR latex
  - Initiate polymerisation by adding TEPA
  - MMA grafted latex
  - Coagulate in hot water containing CaCl₂
  - Coagulum
  - Process: Wash, crumb, dry, bale
  - MG rubber
<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical modification</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical</td>
<td>Reason</td>
<td>≥2%</td>
<td></td>
</tr>
<tr>
<td>Add methyl methacrylate monomer to NR latex</td>
<td>Ammonium olate</td>
<td>Stabilise MMA emulsion in the latex</td>
<td>No</td>
<td>Ammonium olate mixed with MMA monomer and added with organic peroxide to the latex</td>
</tr>
<tr>
<td></td>
<td>Methyl methacrylate monomer (MMA)</td>
<td>To graft PMMA onto NR</td>
<td>Yes</td>
<td>Yes&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Organic peroxide (t-BuOOH)</td>
<td>To act as part of the initiator for polymerisation</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Polymerisation of MMA and formation of graft copolymer</td>
<td>Tetraethyl-pentamine (TEPA)&lt;sup&gt;6&lt;/sup&gt;</td>
<td>Initiate decomposition of peroxide and hence polymerisation</td>
<td>Yes</td>
<td>TEPA added to latex</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Calcium chloride</td>
<td>Aid coagulation</td>
<td>No</td>
<td>Grafted latex added to hot water containing calcium chloride</td>
</tr>
</tbody>
</table>

Remaining concentration of added chemicals:

- Ammonium olate: < 0.01% w/w
- Methyl methacrylate monomer (MMA): <0.001% w/w
- Organic peroxide (t-BuOOH): none remaining (all decomposed)
- Tetraethyl-pentamine: Reacted to give ill-defined mixture of imides

<sup>5</sup> Although the PMMA content of MG rubber is substantial, typically 30 or 40% w/w, the extent of modification of rubber chains is very low. The PMMA is a high molecular weight polymer and is connected to a rubber chain only at one end. There are therefore few modified units on the rubber chains, typically an average of only three per chain; this represents only about an average of 0.01% of the units of a rubber chain.

<sup>6</sup> In promoting the decomposition of the t-BuOOH, tetraethyl-pentamine (TEPA) reacts with it and an amine function is reduced to an imide function. TEPA is multifunctional in amine and the result is a mixture of chemicals with differing levels of amine and imine. Much of these are removed during coagulation and washing.
• Calcium chloride: negligible (washed out)

REACH implementation/actions:

For **PMMA, if it exceeds 1 ton/year per importer, registration is required.** Since PMMA is a polymer, it is the **monomer unit (MMA)** that needs to be registered.

For **tetraethyl-pentamine (TEPA) and methyl methacrylate monomer**, since the amounts of chemical modification are above the 2% threshold, the monomer units, which remain bound in the polymer, need to be registered if the total annual quantity per importer exceeds 1 ton.

Registration is not required for ammonium oleate which can only be present as an impurity coming from the previous grafting process.
4.6. **SP/PA Rubber (Superior processing/Process Aid)**

Superior Processing and Process Aid rubbers were developed in the 1950’s to offer improved processing of rubber compounds, particularly in extrusion. They comprise a mixture of natural rubber latex and PreVulcanised (PV) natural rubber latex in varying ratios. The crosslinked particles from the prevulcanised latex are dispersed in the normal natural rubber and act to change the processing behaviour, particularly of compounds containing low levels of reinforcing filler or non-reinforcing filler. One advantage of the use of these rubbers is much improved finish of extrusions.

The residual chemicals will depend on the formulation of the prevulcanised latex used; there may be differences in accelerators and whether or not antioxidant is added. The following is an example.

![Diagram of SP/PA rubber processing](image-url)
<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical Reason</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounding</td>
<td>Sulphur</td>
<td>Crosslink the rubber in the latex</td>
<td>Yes/No</td>
<td>Addition of rubber curative chemicals</td>
</tr>
<tr>
<td></td>
<td>Zinc dialkyl dithiocarbamate</td>
<td>Accelerator for crosslinking process</td>
<td>Yes/No</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zinc oxide</td>
<td>Activator for crosslinking process</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Antioxidant</td>
<td>To stabilise against oxidation</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Maturation</td>
<td>None</td>
<td></td>
<td></td>
<td>In process PV latex</td>
</tr>
<tr>
<td>Stabilisation</td>
<td>Potassium laurate</td>
<td>Stabilise the latex as a colloid</td>
<td>No</td>
<td>Addition of potassium laurate</td>
</tr>
<tr>
<td>Blend with NR latex</td>
<td>None</td>
<td></td>
<td></td>
<td>Mixing NR and PV latices</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Formic acid</td>
<td>Coagulate the latex blend</td>
<td>No</td>
<td>Add formic acid</td>
</tr>
<tr>
<td>Process</td>
<td>None</td>
<td></td>
<td></td>
<td>SP or PA rubber</td>
</tr>
</tbody>
</table>

Remaining concentration of added chemicals:

- Sulphur: None remaining, the sulphur is bound to the rubber
- Zinc dialkyl dithiocarbamate: <0.3% w/w
- Zinc oxide: <0.3% w/w
- Antioxidant: <0.5% w/w
- Potassium laurate: <0.1% w/w
- Formic acid: < 0.001 % w/w

REACH implementation/actions:

It is necessary to register the residual accelerator (zinc dialkyl dithiocarbamate, in this example), zinc oxide and antioxidant (if used), if the quantity of each chemical for each importer exceeds 1 ton/year. Potassium laurate is exempt from registration.
4.7. **Epoxidised Natural Rubber (ENR)**

Partial epoxidation of the natural rubber produces a range of materials, which are currently marketed at 25mole% and 50mole% levels of modification. Properties such as oil resistance, dynamic properties and polarity are changed without losing the inherent high strength of natural rubber.

The modification is effected in latex by performic acid but this is unstable and is formed in equilibrium with the added reagents, formic acid and hydrogen peroxide.
60% NR latex concentrate

Stabilise with non-ionic surfactant

Stabilised latex

Add formic acid and hydrogen peroxide

Compounded latex

Heat and maintain reaction temperature

In process ENR

Neutralise with ammonia

ENR latex

Heat coagulate

ENR coagulum

Wash, soak in dilute sodium carbonate

Washed coagulum

Process: Wash, crumb, extrude, dry, bale

ENR rubber
<table>
<thead>
<tr>
<th>Step</th>
<th>Added Substance</th>
<th>Chemical</th>
<th>Physical process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chemical</td>
<td>Yes/no</td>
<td>≥2</td>
</tr>
<tr>
<td>Stabilise</td>
<td>Non-ionic surfactant</td>
<td>Stabilise the latex to allow formic acid to be added</td>
<td>No</td>
<td>Addition of aqueous solution of non-ionic surfactant</td>
</tr>
<tr>
<td>Addition of reagents</td>
<td>Formic acid and hydrogen peroxide</td>
<td>These will form performic acid to react with the NR</td>
<td>No</td>
<td>Addition of formic acid and hydrogen peroxide</td>
</tr>
<tr>
<td>Reaction</td>
<td>None</td>
<td>Formation of performic acid and reaction with NR</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Neutralise</td>
<td>Ammonia</td>
<td>Neutralise the formic acid</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Coagulation</td>
<td>None</td>
<td></td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Wash and soak</td>
<td>Sodium carbonate</td>
<td>Stabilise the ENR</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Process</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remaining concentration of added chemicals:

- **Non-ionic surfactant:** <0.2% w/w
- **Formic acid:** None remaining, neutralised with ammonia and should any remain it would be removed during soaking in aqueous sodium carbonate
- **Hydrogen peroxide:** None remaining, residue from the reaction is destroyed during coagulation.
• Ammonia: None remaining, only sufficient added to neutralise the formic acid and, if there was any excess, it would be removed in the heat coagulation, washing and drying.
• Sodium carbonate: <0.2% w/w

**REACH implementation/actions:**

The only substances of interest for the analysis of this case study are formic acid and hydrogen peroxide which react in order to form performic acid to chemically modify natural rubber by more than 2%. However, it is not possible to isolate performic acid for testing and the modification is effectively limited to the addition of oxygen to double bonds of natural rubber. Registration of none of these substances is required since oxygen, which remains chemically bound, is exempt from registration and neither formic acid nor hydrogen remain in the final product.

Sodium carbonate is exempt because it is added as a stabiliser to protect the ENR from attack by acids. The remaining concentration does not compromise the classification of Epoxidised Natural Rubber.
References


