



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 registration¹, but the exemption is not extended to the monomer units for which registration is required.

As explained in the ECHA's guidance² 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.**

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 catalysts 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 V³, 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.

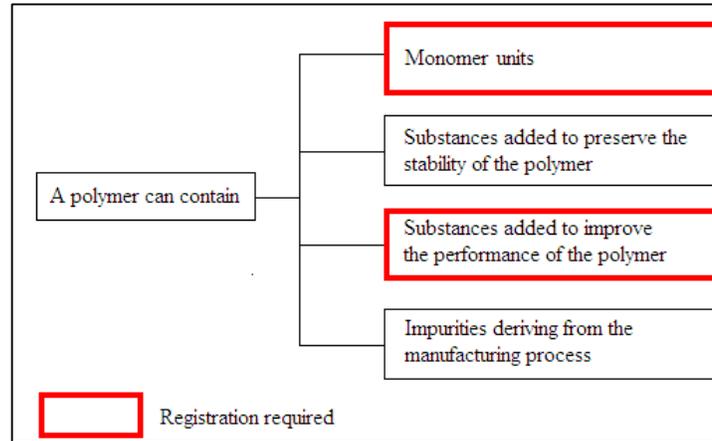


Figure 1.1: What need to be registered in a synthetic polymer.

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 $\geq 2\%$ w/w chemically-bound).

2. Assessment methodology and decisional flow-chart

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

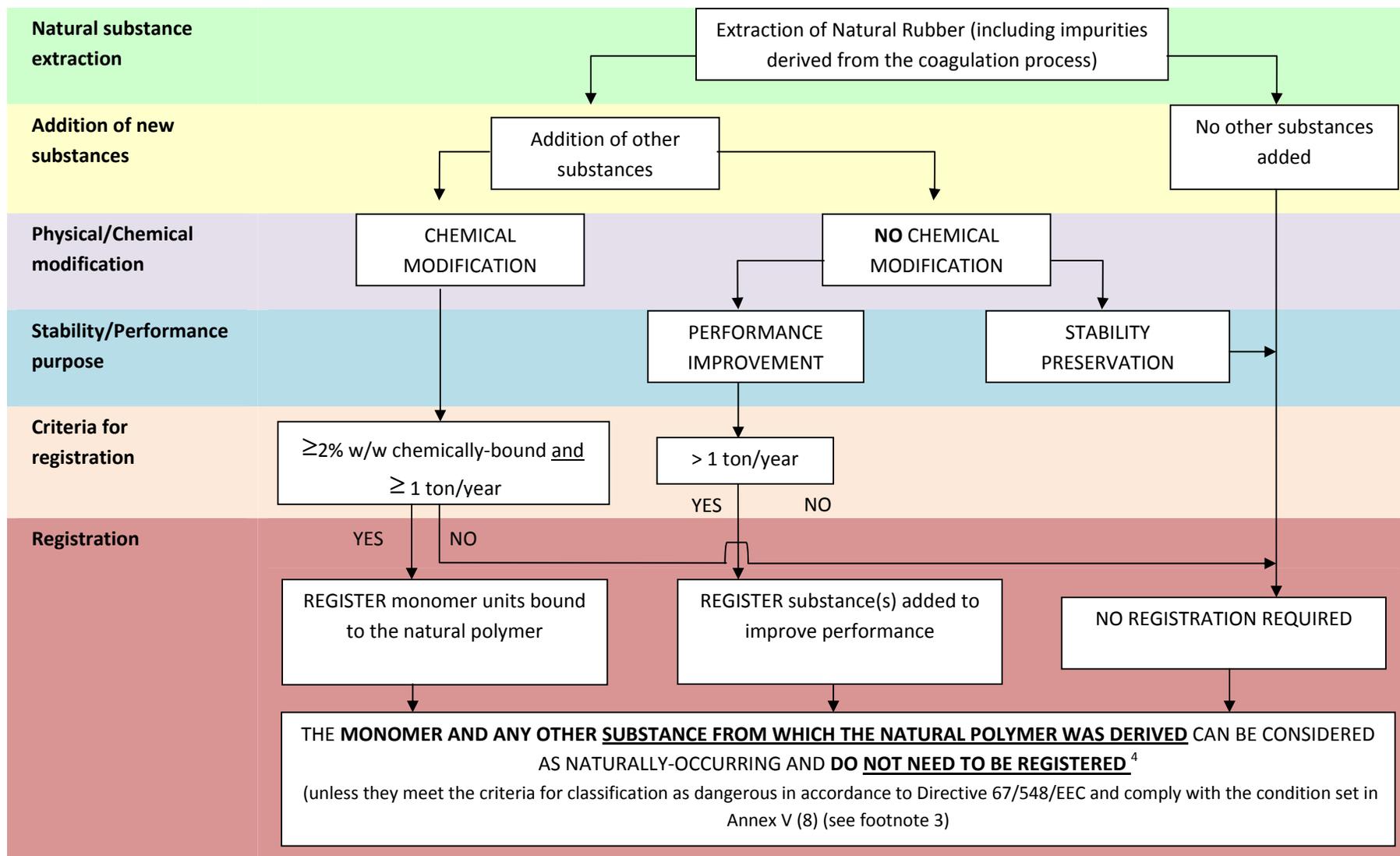
8. *Substances which occur in nature other than those listed under paragraph 7, if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC or unless they are persistent, bioaccumulative and toxic or very persistent and very bioaccumulative 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.

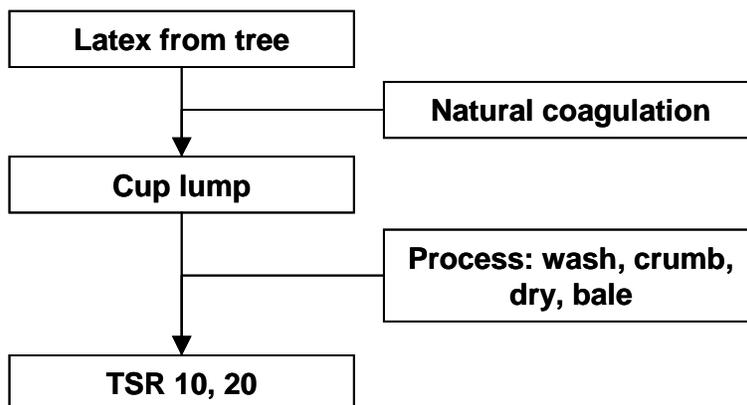
- **Registration is required for added substances when:**
 - Substances are added to improve the performance of natural rubber and the presence of each exceeds 1 ton/year per importer.

- **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.



3. Case Studies 1: Natural Rubber – non-treated grades

3.1. TSR 10, TSR 20

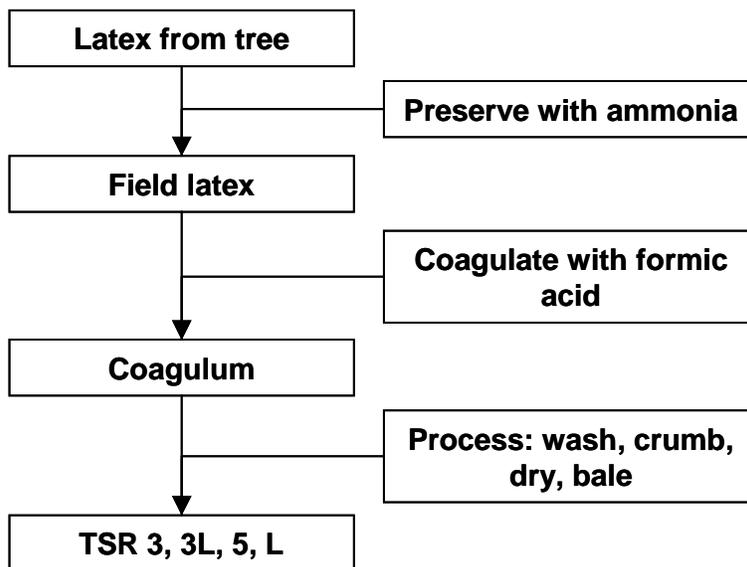


Step	Added Substance		Chemical modification		Physical process	Product
	Chemical	Reason	Yes/no	≥2%		
Natural coagulation	-	-	NO	-	Coagulation	Coagulum
Processing	-	-	NO	-	Washing, crumbing, drying, baling	TSR 10, 20

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)



Step	Added Substance		Chemical		Physical process	Product
	Chemical	Reason	Yes/no	≥2%		
Preserve	Ammonia	Prevent autocoagulation during transportation etc	No	-	Ammonia added to collected latex	Field latex
Coagulation	Formic acid	Neutralise ammonia and coagulate latex	No	-	Formic acid added to latex	Coagulum
Processing	-	-	No	-	Washing, crumbing (optional), drying, baling	TSR 3, 3L, 5, L

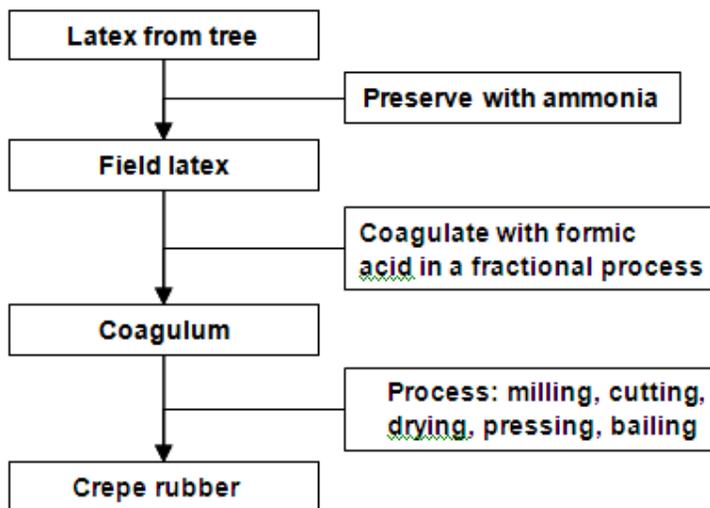
Concentration of impurities remaining in the final product:

- 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



Step	Added Substance		Chemical		Physical process	Product
	Chemical	Reason	Yes/No	≥2%		
Preserve	Ammonia	Prevent autocoagulation during transportation etc	No	-	Ammonia added to collected latex	Field latex
Coagulation	Formic acid	Neutralise ammonia and coagulate latex	No	-	Formic acid added to latex	Coagulum
Processing	-	-	No	-	Milling, cutting, drying, pressing, baling	Crepe Rubber

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

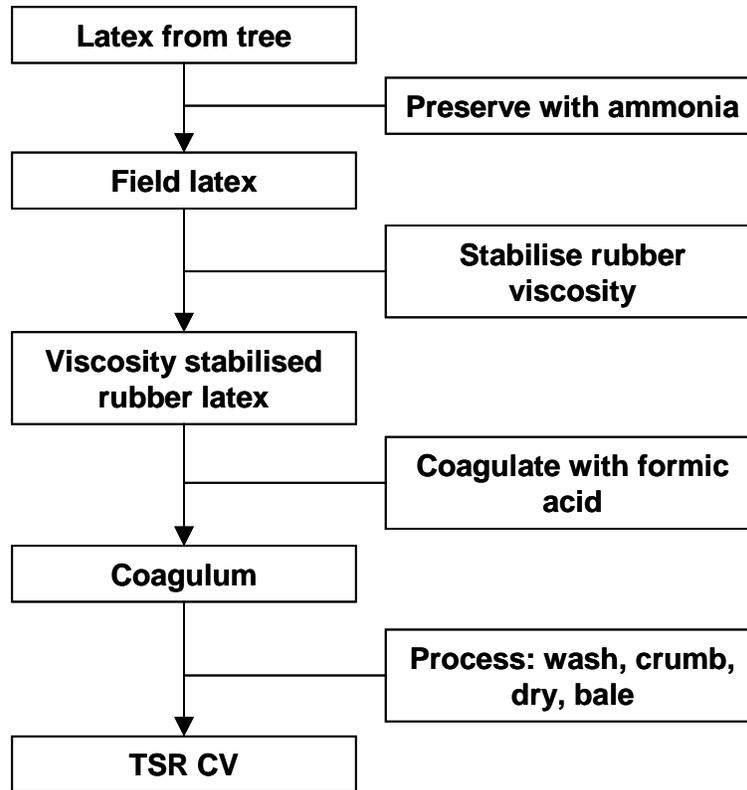
from the preservation/coagulation process which do not make the substance classifiable according to Directive 67/548/EEC.

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)



Step	Added Substance		Chemical modification		Physical process	Product
	Chemical	Reason	Yes/no	≥2%		
Preserve	Ammonia	Prevent autocoagulation during transportation etc	NO	-	Ammonia added to collected latex	Field latex
Stabilise rubber viscosity	Hydroxyl-amine neutral sulphate	Preserve the viscosity of the rubber	YES	NO	Hydroxyl-amine neutral sulphate added to latex	Latex with viscosity stabilised rubber
Coagulation	Formic acid	Neutralise ammonia and coagulate latex	NO	-	Formic acid added to latex	Coagulum
Processing	-	-	NO	-	Washing, crumbing, drying, baling	TSR 3, 3L, 5, L

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

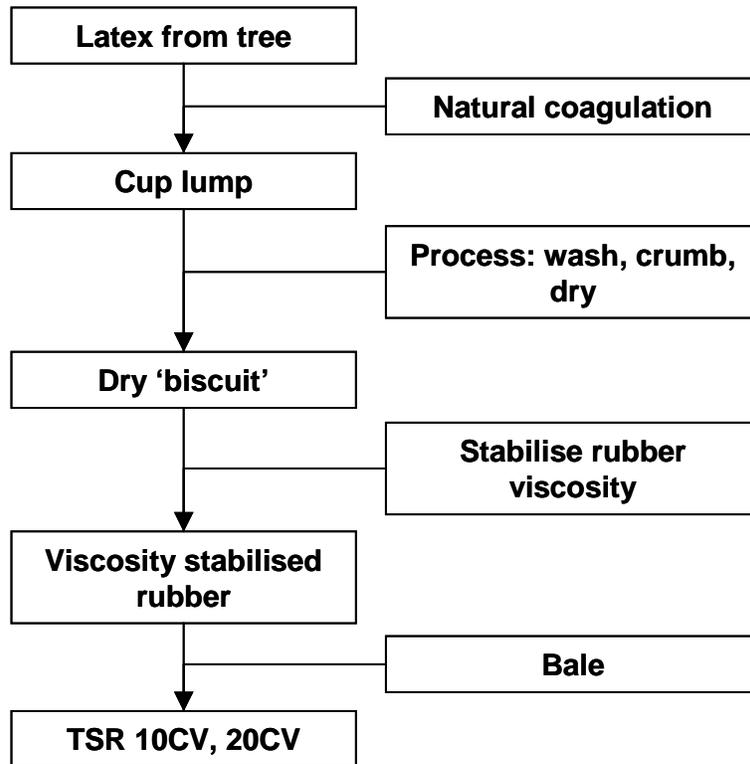
REACH implementation/actions:

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)



Step	Added Substance		Chemical		Physical process	Product
	Chemical	Reason	Yes/no	≥2%		
Stabilise rubber viscosity	Hydroxyl-amine neutral sulphate	Preserve the viscosity of the rubber	Yes	No	Hydroxyl-amine neutral sulphate added to dried rubber in extruder	Viscosity stabilised rubber
Bale	-	-	NO	-	Physical compaction	TSR 10 CV, 20 CV

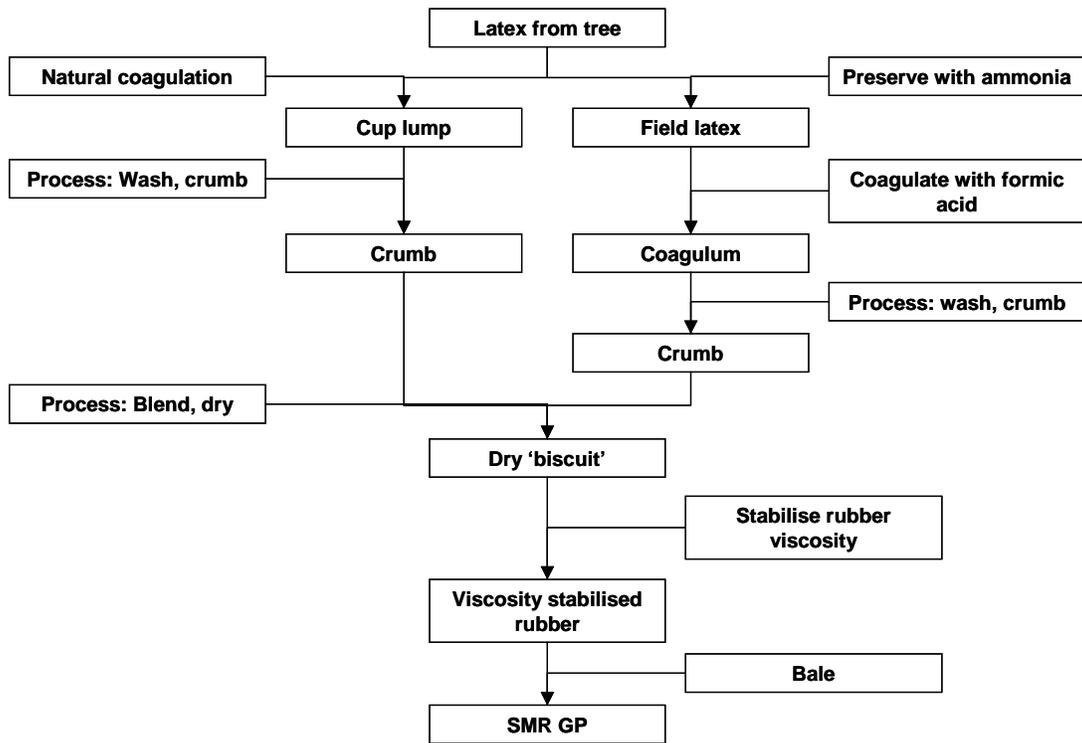
Concentration of impurities remaining in the final product:

- 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



Step	Added Substance		Chemical		Physical process	Product
	Chemical	Reason	Yes/no	≥2%		
Natural coagulation	-	-	No	-	Coagulation	Coagulum
Preserve	Ammonia	Prevent autocoagulation during transportation etc	No	-	Gaseous ammonia added to collected latex	Field latex
Coagulation	Formic acid	Neutralise ammonia and coagulate latex	No	-	Formic acid added to latex	Coagulum
Stabilise rubber viscosity	Hydroxyl-amine neutral sulphate	Preserve the viscosity of the rubber	Yes	No	Hydroxyl-amine neutral sulphate added to dried rubber in extruder	Viscosity stabilised rubber
Processing	-	-	No	-	Washing, crumbing, drying, baling	Dry 'biscuit'
Bale	-	-	No	-	Physical compaction	SMR GP

Concentration of impurities remaining in the final product:

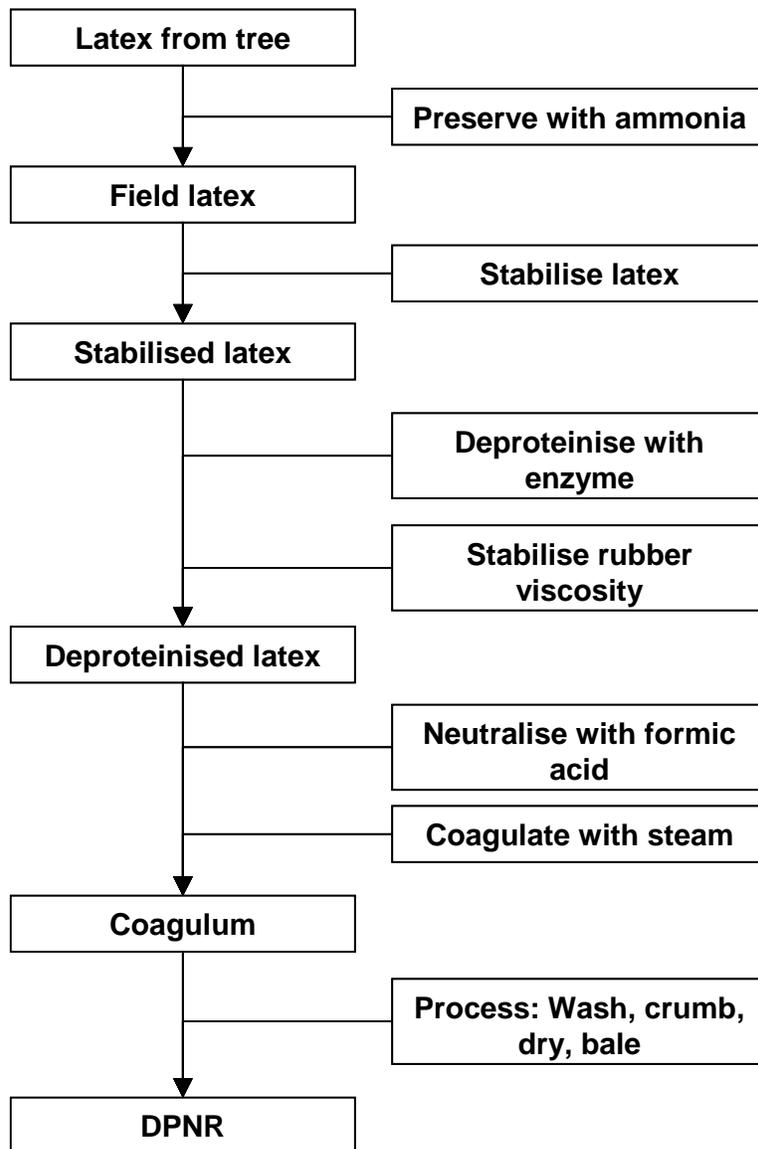
- Ammonia: none remaining (neutralised by formic acid)
- Formic acid: <0.01% w/w
- Hydroxylamine neutral sulphate: <0.03% w/w

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.



Step	Added Substance		Chemical		Physical process	Product
	Chemical	Reason	Yes/no	≥2%		
Preserve	Ammonia	Prevent autocoagulation during transportation etc	No	-	Gaseous ammonia added to collected latex	Field latex
Stabilise latex	Teric N10 ⁶	Prevent coagulation during enzyme treatment	No	-	Non-ionic surfactant added to latex	Stabilised latex
Deproteinise	Protease enzyme protein	Digest protein in the latex	NO	-	Enzyme added to the latex	Low protein latex
Stabilise rubber viscosity	Hydroxylamine neutral sulphate	Preserve the viscosity of the rubber	Yes	No	Hydroxylamine neutral sulphate added to latex	Viscosity stabilised rubber
Coagulation with steam	-	-	No	-		Coagulum
Processing	-	-	No	-	Washing, crumbing, drying, baling	DPNR

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:

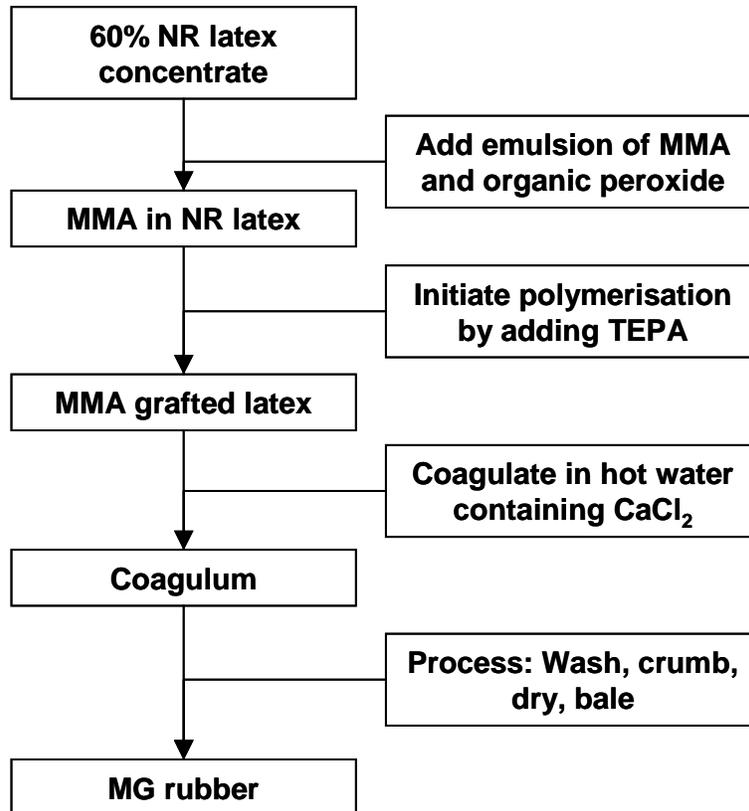
Registration is not required for any of the substances involved.

For hydroxylamine neutral sulphate see case study 4.1.

For teric N10⁴, 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.

⁴ Polyoxyethylene 10 phenol ether

4.5. MG Rubber (Methacrylate grafted rubber)



Step	Added Substance		Chemical modification		Physical process	Product
	Chemical	Reason	Yes/no	≥2%		
Add methyl methacrylate monomer to NR latex	Ammonium oleate	Stabilise MMA emulsion in the latex	No		Ammonium oleate mixed with MMA monomer and added with organic peroxide to the latex	NR latex with MMA swollen into the rubber
	Methyl methacrylate monomer (MMA)	To graft PMMA onto NR	Yes	Yes ⁵		
	Organic peroxide (t-BuOOH)	To act as part of the initiator for polymerisation	No			
Polymerisation of MMA and formation of graft copolymer	Tetraethyl-pentamine (TEPA) ⁶	Initiate decomposition of peroxide and hence polymerisation	Yes	Yes	TEPA added to latex	Latex with PMMA grafted onto NR
Coagulation	Calcium chloride	Aid coagulation	No		Grafted latex added to hot water containing calcium chloride	Coagulum of graft copolymer

Remaining concentration of added chemicals:

- Ammonium oleate: < 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

⁵ 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.

⁶ 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.

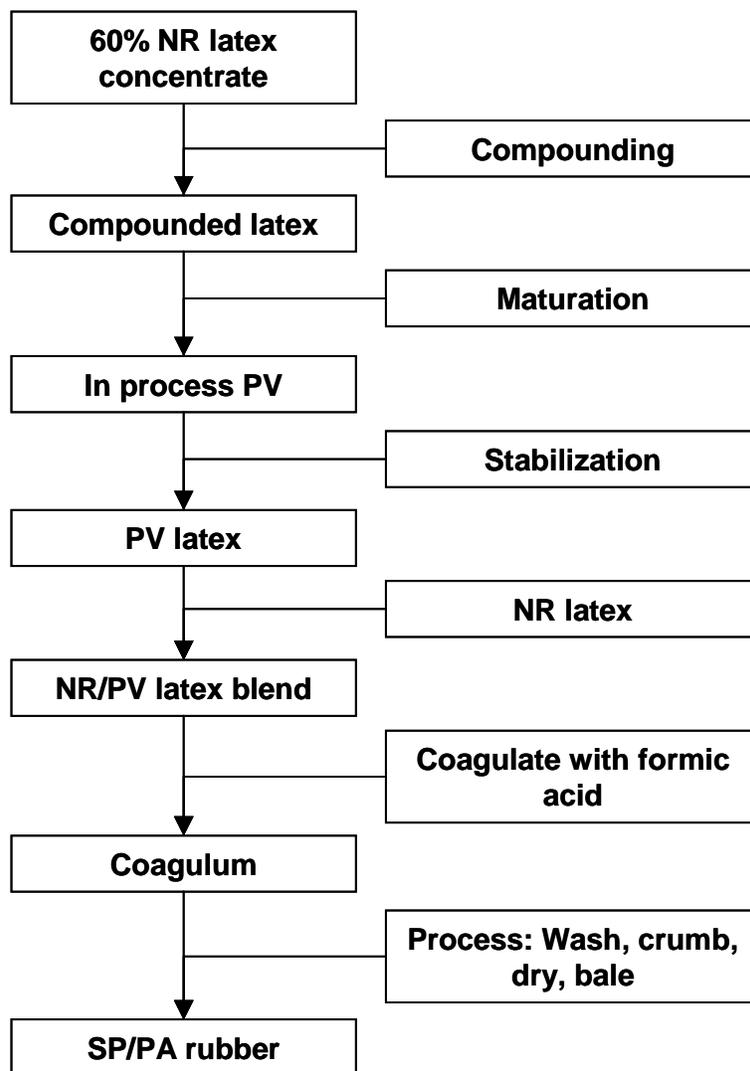
For **tetraethyl-pentamine (TEPA) and methyl methacrylate monomer**, since the amounts of chemical modification are above the 2% threshold, the monomer units, which remain bound in the polymer, need to be registered if the total annual quantity per importer exceeds 1 ton.

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.



Step	Added Substance		Chemical		Physical process	Product
	Chemical	Reason	Yes/no	≥2		
Compounding	Sulphur	Crosslink the rubber in the latex	Yes	No	Addition of rubber curative chemicals	Compound latex
	Zinc dialkyl dithiocarbamate	Accelerator for crosslinking process	Yes	No		
	Zinc oxide	Activator for crosslinking process	No			
	Antioxidant	To stabilise against oxidation	No			
Maturation	None					In process PV latex
Stabilisation	Potassium laurate	Stabilise the latex as a colloid	No		Addition of potassium laurate	PV latex
Blend with NR latex	None				Mixing NR and PV latices	Latex blend
Coagulation	Formic acid	Coagulate the latex blend	No		Add formic acid	Coagulum
Process	None					SP or PA rubber

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

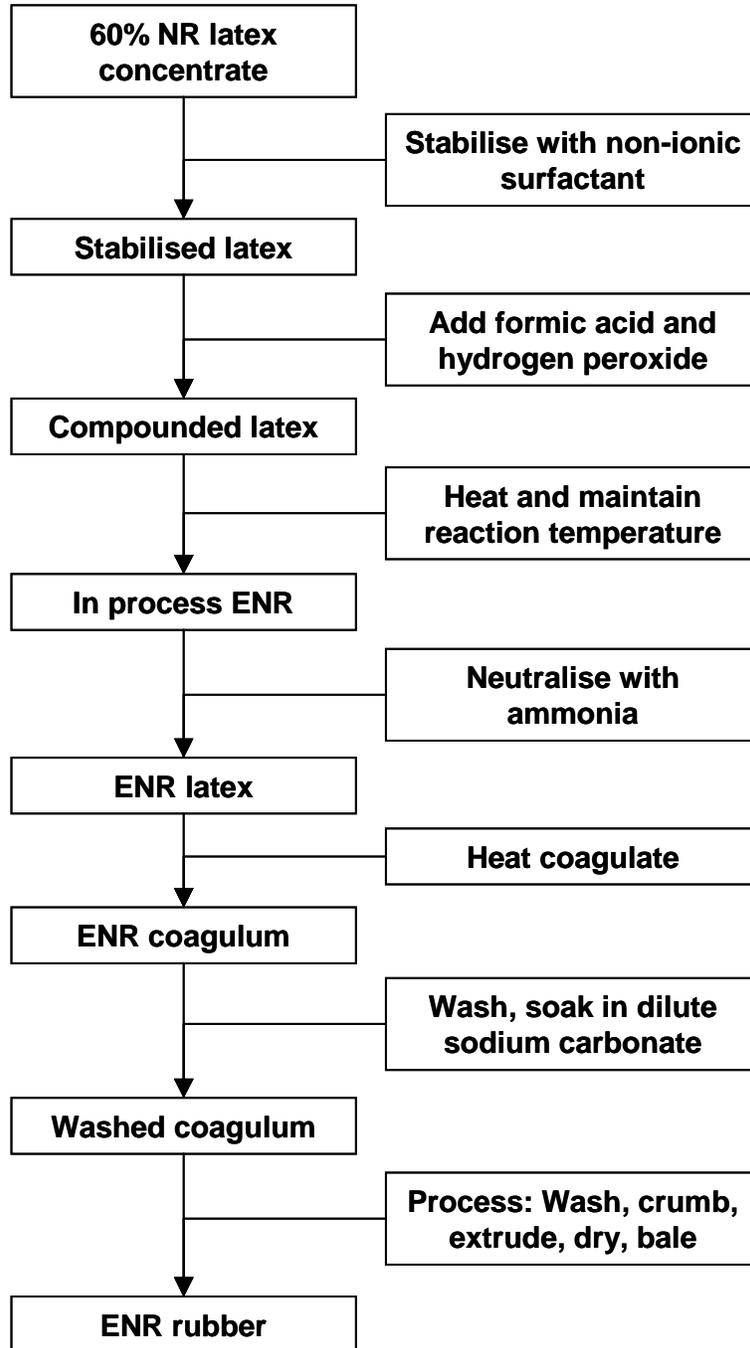
REACH implementation/actions:

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.



Step	Added Substance		Chemical		Physical process	Product
	Chemical	Reason	Yes/no	≥2		
Stabilise	Non-ionic surfactant	Stabilise the latex to allow formic acid to be added	No		Addition of aqueous solution of non-ionic surfactant	Stabilised latex
Addition of reagents	Formic acid and hydrogen peroxide	These will form performic acid to react with the NR	No		Addition of formic acid and hydrogen peroxide	Compounded latex
Reaction	None	Formation of performic acid and reaction with NR	Yes	Yes	Heat compounded latex and maintain at reaction temperature	In process ENR latex
Neutralise	Ammonia	Neutralise the formic acid	No		Add sufficient ammonia to neutralise	ENR latex
Coagulation	None		No		Use steam to heat coagulate the latex	Coagulum
Wash and soak	Sodium carbonate	Stabilise the ENR	No		Wash with water and soak in dilute aqueous sodium carbonate	Stabilised ENR
Process	None				Wash, extrude, dry	ENR

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

- **ECHA 2008.** *Guidance for monomers and polymers.* Guidance for the implementation of REACH. May 2008.
http://reach.jrc.it/docs/guidance_document/polymers_en.pdf
- **REACH 2006.** REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 December 2006 concerning the *Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)*, establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.
<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:396:0001:0849:EN:PDF>
- European chemical Substances Information System
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- Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations.
<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1999:200:0001:0068:EN:PDF>
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<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31967L0548:EN:HTML>