

Reclaim from Rubber Resources free of Polycyclic Aromatic Hydrocarbons and N-Nitrosamines

Abstract

Rubber Resources is a company specialising in recycling rubber waste into products that can be re-used for the production of consumer goods and products for commercial markets.

We have two separate production processes. One is for the production of Natural Rubber reclaim, for which mainly truck tyre tread peelings are used, and a second one is for production of Butyl reclaim, for which inner-tubes are used. Particularly for the European market, the Natural Rubber process has specific conditions to ensure that the reclaim meets European environmental and human health legislations. Alongside our concern for quality in general, we feel that our role in recycling requires additional efforts to protect the environment and human health. We maintain strict health and safety standards, both for our employees and for society as a whole, and our products are tested for various health and environmental aspects.

Two aspects of major concern to us are Polycyclic aromatic oils and N-Nitrosamines.

Polycyclic aromatic Hydrocarbons.

The European directive 2005/69/EC restricts the use of certain PAHs in extender oils used in tyre production. The directive applies to tyres produced after 1 January 2010.

Our reclaim is supplied for all kinds of rubber compounds. While reclaim is also supplied for tyre compounds in Europe, the PAH restriction is relevant to us.

We have tested Butyl reclaim and our Natural Rubber reclaim (for the European market) in accordance with the test method stated in the European Directive.

Test results have shown that the content of PAHs in both reclaims meets the specification in the directive. Both reclaims from Rubber Resources may be used in the market for the production of tyres or parts of tyres and for treads for retreading without limitations arising from Directive 2005/69/EC.

N-Nitrosamines.

There is not currently a restricting directive for N-Nitrosamines in the rubber industry, only an environmental guideline which states that the total amount of N-Nitrosamines in the atmosphere must be below 1 µg/m³. To meet this guideline the rubber industry prefers its raw materials to be free of N-Nitrosamine generation. We have tested our reclaim, by simulation using reclaim in the tyre industry. We have tested Natural Rubber reclaim for the European market and Butyl reclaim.

Results have shown that no N-Nitrosamines are formed during handling, processing and curing of the reclaim. Thus we can state that, with regard to the absence of N-Nitrosamines, both reclaims from Rubber Resources will not have a negative effect on the environment or on the health of employees in the rubber industry.

Due to the combination of the choice of raw materials and the specific processing conditions, Rubber Resources can guarantee that their Natural Rubber reclaim for the European market as well as their Butyl reclaim are of a consistent quality and therefore meet the regulations for PAHs and N-Nitrosamines at all times.

Reclaim from Rubber Resources free of Polycyclic Aromatic Hydrocarbons

(Anita Hendriks, October 2006)

Introduction.

Polycyclic Aromatic Hydrocarbons are naturally-occurring substances formed whenever carbon-containing compounds are burned at low temperatures in uncontrolled conditions.

PAHs are produced in forest fires and volcanoes; in human activities such as tobacco smoking; in home heating and power generation; in cooking food and waste incineration; and in a number of industrial processes.

PAHs occur naturally in crude-oil and, being easily formed and stable, accumulate during the early stages of cracking and distillation of the oil.

This process of partial oxidation results in a mixture of components with linked unsaturated five- and six-member carbon rings, called the Polycyclic Aromatic Hydrocarbons.

The individual characteristics of PAHs cannot be easily determined. However, as some can be shown to be carcinogenic to animals, it is reasonable to classify the mixtures of PAHs as likely to cause cancer in humans. Oils known to contain PAHs therefore require risk and safety labelling¹. Processes likely to release PAHs into the environment should be controlled and avoided.

One such process is the use of extender oils in tyre compounds. Rubber compounds require extender oils to facilitate processing. In the tread compound the oil is also an essential component for the technical performance of the tyre, in particular for its road adherence (or grip) properties and wear and endurance characteristics.

Highly aromatic oils (DAE, Distillate aromatic extract oils) have traditionally been used in tyres because of the excellent compatibility with natural and synthetic rubbers and also because of their low market prices.

In 2005 the European Commission adopted a Directive² restricting the marketing and use of certain PAHs in extender oils used in tyre production. Tyres produced after 1 January 2010 have to comply with the requirements of the Directive.

In the Directive a list is mentioned of eight different PAHs which the European Union has classified as carcinogenic. One specific PAH, benzo(a)pyrene (BaP), is proposed as a qualitative and quantitative marker for the presence of other PAHs.

Extender oils may not be used for the production of tyres if they contain more than 1 mg/kg BaP and/or more than 10 mg/kg of the sum of all listed PAHs. These limits are regarded as maintained, if the polycyclic aromatics extract is less than 3% by mass, as measured by standard method IP346³.

Tyres and treads for retreading may not contain extender oils exceeding the limits indicated above. These limits are regarded as maintained, if the vulcanised rubber compounds do not exceed the limit of 0.35% Bay protons as measured by ISO 21461⁴.

Currently two alternative oils are mainly available which meet the requirements of Directive 2005/69/EC: MES (Mild extract solvates) and TDAE (Treated distillate aromatic extracts). The tyre industry, which is actively involved in development of alternative oils, has to adjust all its tyre compounds to safeguard tyre performance. Characteristics of concern are mainly wet grip, wear and endurance.

Rubber reclaim can be used in all kinds of tyre compounds. Butyl reclaim, based on butyl inner-tubes, is mainly advised for use in the inner-liner compound. Natural rubber reclaim, based on truck tread material, can be used in several tyre compounds like treads and carcass compounds.

Results

Because rubber reclaim is used for tyre compounds in Europe, it has to meet the regulations in Directive 2005/69/EC. Rubber Resources has the reclaim tested in accordance with the method mentioned in the Directive for vulcanised rubber compounds (ISO 21461). Natural Rubber reclaim for the European market and Butyl reclaim are tested. The analysis is done by an independent research institute in Germany, the DIK⁵.

Test methodology

Analysis according to ISO 21461 is described as follows:

The rubber material is cut into small pieces and is extracted using acetone for 8 hours in a soxhlet apparatus. After drying by a stream of nitrogen the dried extract is solved in methylene chloride. The methylene chloride solution is prepared using a clean-up step by means of solid phase extraction. The dried non-polar eluate of the solid phase extract is used for the NMR spectroscopy. With NMR spectroscopy the percentage of Bay Region Hydrogens (% H_{bay}) is determined. This gives an indication of the aromaticity of the used oil.

Sample	% Bay Region Hydrogens
Natural rubber reclaim	0,13 %
Butyl reclaim	0,12 %

Conclusion

According to Directive 2005/69/EC a vulcanised rubber compound may be placed on the market for the production of tyres or parts of tyres, if the percentage of Bay Region Hydrogens (H_{bay}) is below 0.35%. The limitations for Benzo(a)pyrene and the sum of all listed PAHs are regarded as maintained.

Natural rubber reclaim (for the European market) and Butyl reclaim, both from Rubber Resources, meet the specifications in the Directive. Both reclaims from Rubber Resources may be used in the market for the production of tyres or parts of tyres and for treads for retreading without limitations arising from Directive 2005/69/EC.

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1. Risk phrase R45 (may cause cancer) and Safety label T (toxic)
 2. Directive 2005/69/EC, 15 November 2005.
 3. Institute of Petroleum standard IP346 - Dimethyl-Sulfoxide extraction refractive index method.
 4. ISO 21461 - Determination of aromaticity of oil in vulcanised rubber compounds – NMR analyses.
 5. Deutsche Institut für Kautschuk technologie, Hannover.

Reclaim from Rubber Resources free of N-Nitrosamine

Introduction

Nitrosamines were first described in chemical literature over 100 years ago, but not until 1956 did they receive much attention. In that year two British scientists reported that dimethylnitrosamine produced liver tumours in rats⁶. This discovery, made during a routine screening of chemicals, caused scientists around the world to investigate the carcinogenic properties of other nitrosamines. Many nitrosamines have been found to be carcinogenic in a wide variety of experimental animals. Reliable analytical methods to determine nitrosamine levels were developed during the 1970s. Detecting low levels of nitrosamines has been possible since then.

Nitrosamines have the chemical structure $RR'N-NO$, where R and R' can be an aliphatic or aromatic group. Nitrosamines of concern are derived from secondary amines. Primary amines do not produce stable nitrosamines and tertiary amines do not readily form nitrosamines. It is especially the aliphatic nitrosamines, like NDMA (nitrosodimethylamine), which are carcinogenic for a range of animals⁷. The reaction of generating nitrosamines is dependent on temperature, humidity and pH value. In rubber manufacturing nitrosamine formation occurs during the cure, storage and subsequent treatment of rubber products.

For the generation of nitrosamines the simultaneous presence of a secondary amine, $RR'-NH$, and a nitrating agent, $NxOy$, is necessary. The prime sources of secondary amines in rubber are certain accelerators and sulphur donors. Other ingredients, such as amine antioxidants and the raw polymers, also need to be considered. Natural rubber is completely free of nitrosamines, but this is not true for all synthetic rubbers. For example, SBRs containing nitrites as polymerisation short-stops give rise to excessive nitrosamine levels.

Nitrating agents are descended from carbon black, silica, salt baths and from the air.

Current legislation restricting nitrosamine levels only apply to two products: baby bottle teats and dummies/pacifiers [2]. Two test methods are used: those of the German Bundesgesundheitsamt (BGA) and the US Food and Drugs Administration (FDA). The BGA test method uses extraction by simulated saliva, whereas the FDA procedure uses dichloromethane. The thermal energy analyser (TEA) is used in each case for determination of the nitrosamines. The former technique is inefficient, but is considered realistic for teats and dummies.

West Germany has also introduced environmental guidelines for atmospheric nitrosamine levels in the manufacturing industry: the amount of nitrosamines should be kept to an absolute minimum, preferably zero. Negotiations with the rubber industry led to a stipulated maximum value of the total amount of Nitrosamines of $1 \mu\text{g}/\text{m}^3$ air. The guideline is described in TRGS 552 (Technische Regeln für Gefahrstoffe) of 1998⁸.

This guideline affects both material suppliers and rubber manufacturers. Suppliers need to show that their products are free from nitrosamines or chemicals leading to their generation. Rubber manufacturers have to devise formulations to meet regulatory limits on nitrosamines and also to ensure that working environments are not contaminated.

Rubber reclaim is supplied to the rubber industry and therefore has to meet the value in the guideline. Nitrosamines may not be formed during processing, treatment and storage.

Results

Test methodology

A rubber reclaim sample is heated under a stream of nitrogen for 15 minutes at 180°C and is allowed to cool under nitrogen for 20 minutes. Nitrogen flow is 1.5 l/minute. The sampling of volatile N-Nitrosamines is carried out by adsorption on thermosorb tubes. For the analyses of the desorbent the GC-TEA coupling is used. This method is used as a simulation of using reclaim for rubber compounds in the tyre industry. It covers the handling, processing and curing of a rubber tyre compound.

Determined are the nine high-volatile N-Nitrosamines mentioned in guideline TRGS 552⁸.

NDMA	N-Nitroso-dimethylamine
NMEA	N-Nitroso-ethylmethylamine
NDEA	N-Nitroso-Diethylamine
NDiPA	N-Nitroso-diisopropylamine
NDPA	N-Nitroso-dipropylamine
NDBA	N-Nitroso-dibutylamine
NPIP	N-Nitroso-piperidine
NPYR	N-Nitroso-pyrrolidine
NMOR	N-Nitroso-morpholine

Detection limit for all high volatile Nitrosamines: $\leq 3,6 \mu\text{g/kg}$
 Determination limit: $\leq 11,0 \mu\text{g/kg}$

The total amount of N-Nitrosamines is calculated. If an N-Nitrosamine is determined, the concentration is put in μg of N-Nitrosamine formed per kg of rubber material.

Tested are Natural Rubber reclaim for the European market and Butyl reclaim, both from Rubber Resources.

	NDMA	NMEA	NDEA	NDiPA	NDPA	NDBA	NPIP	NPYR	NMOR	\sum NA
RBR	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
RNR	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd = not determined

\sum NA = the total amount of the nine high volatile N-Nitrosamines

RBR = Butyl reclaim

RNR = Natural rubber reclaim for the European market

Conclusion

To meet the environmental guideline stated in TRGS 552, the rubber industry prefers reclaim to be free of Nitrosamine generation.

Simulation of using reclaim in the tyre industry shows that no Nitrosamine is generated during handling and curing of the reclaim in a tyre compound.

Results for both tested reclaims show that the amounts of all determined N-Nitrosamines are below the detection limit of the test method.

Thus we can state that, in terms of the absence of N-Nitrosamines, Natural Rubber reclaim (for the European market) and Butyl reclaim, both from Rubber Resources, will not have a negative effect on the environment and on the health of employees in the rubber industry.

⁶ R.A.Scanlan, Oregon State University, (2003), Nitrosamines and Cancer.

⁷ Rubber Consultants, UK, (1990), Nitrosamines and rubber formulations.

⁸ Vorschriftensammlung der Staatlichen Gewerbeaufsicht, (1999), N-Nitrosamine.