

Survey of Chemical Substances in Consumer Products

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Liberation of MBT in natural rubber

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2 Introduction

May 2002 Eurofins Danmark A/S was requested to carry out a project for the Danish Environmental Protection Agency titled:

- *Liberation of MBT in natural rubber*

The Danish Environmental Protection Agency had formulated a project (02/05/02, www.mst.dk/kemi/02050110.htm) that is the basis of the content and scope of the project.

MBT (2-mercaptobenzothiazole) is a typically used accelerator in the production of natural rubber. MBT may cause human allergic reactions for which reason the Danish Environmental Protection Agency wants to test products for migration of this substance. Previously migration of MBT has been determined in soothers¹. The antioxidants BHT and A2246 are added to the product to increase the constancy toward oxidation and weather.

Content analyses are not requested performed of the natural rubber products for which reason only migration test are carried out. The migration test is performed according to the "Final Draft" prEN 1400-3, April 2002². The simulants are analysed for:

- MBT
- MBTS (2-bis-benzothiazole-2,2'-disulfid) – a dimer of MBT that likewise may be used as accelerator.
- The antioxidant BHT (butylated hydroxy toluene)
- The antioxidant A2246 (6,6'-di-t-butyl-2,2'-methylendi-p-cresol)

Project leaders at the Danish Environmental Protection Agency were Frank Jensen and Shima Dobel.

The products included in this project are anonymous in this report. Product references are stated in appendix A.

¹ Soothers and feeding bottles – chemistry and health. The Danish Institute for Institute for Food Inspection and Nutrition, The Danish Department for Food. December 1999.

² FINAL DRAFT. prEN 1400-3. Child use and care articles – Soothers for babies and young children – Part 3: Chemical requirements and tests. April 2002.

3 Mapping

Natural rubber can be naturally produced based on latex from the tree *Hevea brasiliensis*, however, it can also be synthetically produced based on the chemical compound cis-1,4-polyisoprene. Present project does not distinguish between naturally and synthetically produced natural rubbers.

3.1 PRODUCTS FOR INITIAL TESTING

At the market research the following product groups were initially selected for further testing:

- Balloons
- Teething ring
- Space hopper (non-stop balls)
- Eraser
- Soft animals (e.g. spiders, skeletons)
- Soft masks
- Cleaning gloves
- Erotic appliances (dildos and latex cloths)
- Wet and dry suits
- Diving-mask
- Snorkel
- Frogman's feet
- Elastic bandages (sports equipment)

Besides the above mentioned product group the Internet was used for a wide search to look for other relevant products to include in the investigation. There has been a general focus on products for children and products that have contact of long duration with skin i.e. where the exposure is relatively large.

Soothers and teats for feeding bottles have been tested in a former project. Condoms are regulated by the Danish Pharmaceutical Board and are therefore not included in the Danish Environmental Protection Agency's project.

3.2 SELECTION OF PRODUCTS FOR THE PROJECT

All of the commonly used products consisting of natural rubber/latex were selected in co-operation with the Danish Environmental Protection Agency for further testing. The products are balloons, cleaning gloves, and erotic appliances.

3.2.1 Teething rings

The dealers and suppliers of teething rings could inform us that the market was dominated by one brand. These teething rings were informed not to contain natural rubber. Teething rings were thus not selected for further testing.

3.2.2 Space hoppers, non-stop balls

Dealers/suppliers of space-hoppers informed us that they contain natural rubber. Some balls are made from "natural" natural rubber, while others are made from synthetic natural rubber. According to information from one of the suppliers the space-hoppers made from synthetic natural rubber are typically those that are transparent with motives or glitter. Non-stop balls were selected for further testing.

3.2.3 Erasers

Some of the purchased erasers were according to information from the supplier made of PVC. These were not included in the investigation. Despite that it has been impossible to obtain information on the material of the other purchased erasers this product group has been selected for further investigation due to the vast exposure to children. One type of erasers were selected that appeals to children due to figures and colours, one transparent with a motive inside indicating that it might be natural rubber and an eraser at the end of pencils as the users frequently bite the end of a pencil.

3.2.4 Animals and masks

Soft animals and soft masks are only sold in limited volumes. Internet search and supplier contact gave the result that soft animals in latex were very rare. Masks are available to adults (carnival and the likes), however, one dealer assessed that the total sale amounted to 1,000-2,000 annually. Masks for children are sold in limited volumes and predominantly at Shrovetide. Thus, one single mask was selected for further investigation.

3.2.5 Diving equipment

Following a thorough Internet search and contact to diving-equipment dealers the following could be demonstrated: snorkels and masks are made from silicone while the suits are mainly made of neoprene. However, there are some dry suits where there is an option for natural rubber hoods. Frogman's feet are typically a mixture of natural rubber and "hi-tech" polymer or solely "hi-tech" polymer. In co-operation with the Danish Environmental Protection Agency it was assessed that the exposure to natural rubber in connection with diving is minimal, thus diving-equipment was not included in the project.

3.2.6 Sports bandage

The predominant parts of the sold sports bandages are made from neoprene. There are two dominant brands of elastic bandages. One brand does not contain natural rubber while the other brand contains natural rubber fabricate in polyester.

The product group was selected for further investigation.

3.3 SELECTED PRODUCTS

Search on the Internet concluded that there were no other product types that should be included in the investigation.

The following products are selected:

- Balloons (two types)
- Space hopper (non-stop balls) (three types)
- Eraser (three types)
- Soft masks (one type)
- Cleaning gloves (three types)
- Erotic appliances (two kinds of dildos and two types of latex cloths)
- Elastic bandages (one type)

3.4 TEST OF PURCHASE PRODUCTS

The products were purchased and the dealer/importers contacted in preparation for clarifying question on their products. Dealer/importers were asked the name/address of the manufacture, number of sold products in Denmark annually, number of sold similar product types, whether the product consists of natural or synthetic natural rubber, and finally information on market shares.

Generally dealers/importers were unable to state whether the products were made from natural or synthetic natural rubber, just as most have difficulties informing on market shares. Finally single dealers/importers refused to answer.

Generally the products of natural rubber are produced in the Orient. There are, however, some exceptions as there is no received information on single products' manufacture. One of the selected types if balloons are produced in Mexico and the elastic bandage in Danish produced. For the erotic appliances products from the Orient and Denmark have been selected.

For one type of balloons it was informed that approximately there was an annual sale in Denmark of 350.000 bags, this was assessed to correspond to approximately 2% of the market. Simultaneously it was mentioned that sales were decreasing.

It is impossible to give a total assessment for space-hoppers; however, one dealer is currently selling more than 100,000 balls. The market share is not known.

The same is the case for the eraser market, however, based on the data that we obtained the annual sale is approximately 100,000. One should be aware that some of these might be PVC produced.

The major part of the sold elastic bandages is made from neoprene, i.e. a minor part of the total sale of elastic bandages contains natural rubber. It is not possible to estimate how much.

The total sale of masks made from latex is estimated to be around 10,000 masks yearly.

Based on information from dealers/importers of rubber gloves the total market is estimated to be more than 1m sold pair of gloves. One dealer estimated that sales were increasing.

It is not possible to assess the market for erotic appliances; however, when the Internet is used it is evident that there are many players. The two dealers where the dildos were purchased assessed their annual sale to be approximately 15,000 pieces, while their sale of latex cloths was approximately 3,000 pieces annually.

4 Analytical methods

4.1 SAMPLE PREPARATION

All samples are cut to a size where the total surface is exactly 1 dm². For the larger products the sample consisted of one piece where the minor products consisted of several pieces.

In accordance with the Danish Environmental Protection Agency it was decided not to boil the samples before migration, as the samples included in this project are not meant for boiling before use.

4.2 MIGRATION AND ANALYSIS OF SIMULANT

Artificial sweat and spit was used as simulant. Sweat is used for the products elastic bandages, gloves, dildos, latex cloths, and mask.

Spit is used for the products balloons, space-balls, and erasers. The selection of simulant is agreed with the Danish Environmental Protection Agency

The 1 dm² large sample pieces are added synthetic spit and synthetic sweat respectively in an amount corresponding to 2 ml pr. 1 cm², covering the samples completely.

The samples are incubated accordingly at 40°C for 24 hours. The migration test is carried out in duplicate.

Following incubation the simulant is extracted with dichloromethane, dried over water free sulphate and evaporated to dry. The simulant is re-dissolved in acetonitrile, after which the extract is analysed at high-pressure liquid chromatography (HPLC). The extract is analysed for content of MBT, MBTS, BHT, and A2246.

5 Results

The results of the migration tests are stated in the table. The limits of detection for the single components are:

MBT: 2 µg/dm²

BHT: 20 µg/dm²

A2246: 6 µg/dm²

MBT (2-mercaptobenzothiazole) that is a thiol can be converted to the disulphide MBTS (benzothiazole disulphide) at oxidation. Transverse the disulphide in the binding in the MBTS weak and may thus easily be reduced to a corresponding thiol (MBT).

Furthermore, MBT may form the corresponding benzothiazole (BTH not to be displaced with BHT) at hydrolysis in an acid aqueous solution.

MBTS, MBT, and BTH may be formed from other benzothiazole-based thiazols that are likewise used as accelerators. Examples are zinc 2-mercaptobenzothiazole (ZMBT) and sodium 2-mercaptobenzothiazole (NaMBT).

Due to the fact that the redox conditions and the stability conditions are not sufficiently fixed in the applied simulants it is impossible to quantify MBTS. A detection of the substance is therefore stated with an X in the table. For the same reason there is no limit of detection for the substance.

Due to the possibility of reformation of MBT to MBTS and to BTH the result for the migration of MBT may be underestimated. The recovery of MBT was low (50-70% on sweat samples, MBT was not detected in spit samples). The same was the case for A2246 as the recovery was 30-40% for sweat samples. None of the results in the table are corrected for low recoveries. Corresponding low recoveries for the substances have formerly been published for the applied CEN-method (see footnote 1).

TABLE 1. RESULTS FOR ANALYSES OF SIMULANTS FROM THE MIGRATION TESTS. THE USED SIMULANT IS STATED UNDER THE SAMPLE NUMBER. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE GIVEN IN µG/DM².

	1		2		3		4		5	
	Balloon		Balloon		Non-stop ball		Non-stop ball		Non-stop ball	
	Spit		Spit		Spit		Spit		Spit	
2-Mercaptobenzothiazole (MBT)	-	-	-	-	-	-	-	-	-	-
2-bis-benzothiazole-2,2'-disulfid (MBTS)	-	-	-	-	-	-	-	-	-	-
Butylret hydroxytoluen (BHT)	-	-	-	-	-	-	-	-	-	-
6,6'-di-t-butyl-2,2'-methylendi-p-cresol (A2246)	-	-	-	-	-	-	-	-	-	-

∴ Means less than the limit of detection

TABLE 1, CONTINUED. RESULTS FOR ANALYSES OF SIMULANTS FROM THE MIGRATION TESTS. THE USED SIMULANT IS STATED UNDER THE SAMPLE NUMBER. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE GIVEN IN $\mu\text{g}/\text{DM}^2$.

	6		7		8		9		10	
	Eraser		Eraser		Eraser		Elastic bandage		Mask	
	Spit		Spit		Spit		Sweat		Sweat	
2-Mercaptobenzothiazole (MBT)	-	-	-	-	-	-	430	490	-	-
2-bis-benzothiazole-2,2'-disulfid (MBTS)	-	-	-	-	-	-	x	x	-	-
Butyleret hydroxytoluen (BHT)	-	-	-	-	-	-	-	-	-	-
6,6'-di-t-butyl-2,2'-methylendi-p-cresol (A2246)	-	-	-	-	-	-	13	16	-	-

∴ Means less than the limit of detection

TABLE 1, CONTINUED. RESULTS FOR ANALYSES OF SIMULANTS FROM THE MIGRATION TESTS. THE USED SIMULANT IS STATED UNDER THE SAMPLE NUMBER. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE GIVEN IN $\mu\text{g}/\text{DM}^2$.

	11		12		13		14		15	
	Gloves		Gloves		Gloves		Dildo		Cloths	
	Sweat		Sweat		Sweat		Sweat		Sweat	
2-Mercaptobenzothiazole (MBT)	-	-	-	-	170	140	-	-	-	-
2-bis-benzothiazole-2,2'-disulfid (MBTS)	-	-	-	-	x	x	-	-	-	-
Butyleret hydroxytoluen (BHT)	-	-	-	-	-	-	-	-	-	-
6,6'-di-t-butyl-2,2'-methylendi-p-cresol (A2246)	-	-	-	-	-	-	-	-	-	-

∴ Means less than the limit of detection

TABLE 1, CONTINUED. RESULTS FOR ANALYSES OF SIMULANTS FROM THE MIGRATION TESTS. THE USED SIMULANT IS STATED UNDER THE SAMPLE NUMBER. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE GIVEN IN $\mu\text{g}/\text{DM}^2$.

	16				17			
	Dildo				Cloths			
	Sweat				Sweat			
2-Mercaptobenzothiazole (MBT)	-	-	-	-	-	-	-	-
2-bis-benzothiazole-2,2'-disulfid (MBTS)	-	-	-	-	-	-	-	-
Butyleret hydroxytoluen (BHT)	-	-	-	-	-	-	-	-
6,6'-di-t-butyl-2,2'-methylendi-p-cresol (A2246)	-	-	-	-	-	-	-	-

∴ Means less than the limit of detection

6 Summary and conclusion

Migration test has been carried out on natural rubber products in accordance with the "Final Draft" prEN 1400-3, April 2002, where the simulants are analysed for MBT, MBTS and the antioxidants BHT and A2246.

MBT and MBTS have been detected in one sample of cleaning gloves and detections of MBT, MBTS, and A2246 in the sample of elastic bandage. The other samples did not show a migration of the tested substances. The two samples with positive MBT result are both tested with sweat as simulant. As the artificial sweat is acid (pH = 3) it corresponds to the expectation, as MBT is more soluble in acid than in water.

The level for the migration varies. In the simulant for the cleaning gloves 160 $\mu\text{g}/\text{dm}^2$ (average) was detected and MBTS was detected qualitatively. 460 $\mu\text{g}/\text{dm}^2$ (average) MBT was detected in the simulant of the elastic bandage and MBTS was detected qualitatively and the level for A2246 was 15 $\mu\text{g}/\text{dm}^2$ (average). BHT could not be detected in either of the samples.

When the values for the migration of MBT are converted into mg/kg the result may be compared with the values that were found in soothers (see footnote 1). However, there are used different simulants in the two investigations as the project on soothers used water and 3% acetic acid. However, there may be a rough comparison as all simulants are aqueous, and two of which are acid (acetic acid and sweat). The value of cleaning gloves was 80 mg/kg (average) and 120 mg/kg (average) for elastic bandages. Migration of MBT to water and 3% acetic acid was detected from values of 0.16 to 11 mg/kg for soothers, meaning that migration of MBT for gloves and elastic bandage was up to 1000 times larger respectively.

The qualitative information may be underestimated due to generally low recoveries at the method and the possibility for reformation between MBT and MBTS.