Nitrosamine Generating Accelerators in Curing of Rubber

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Abstract—Most of the conventional Rubber Accelerators used for curing of rubber produce Nitrosamine during and after processing (during storage). This review is to identify these accelerators and sort out the possible options to replace them with no or less producing Nitrosamine Accelerators.

Keywords: Nitrosamine, Curing of Rubber

I. INTRODUCTION

Nitrosamines, although discovered over 100 years ago, have been under great scrutiny since1956 when it was reported by two British scientists that N-nitrosodimethylamine (NDMA) caused the formation of liver tumors in laboratory rats. As it turns out, the discovery was made while testing NDMA (N-Nitrosodimethylamine) as a proposed solvent for the use in the dry- cleaning industry. It was not until the 1980's that testing equipment was developed that was capable and robust enough to detect the impact of nitrosamines. Since that time, more than 90% of the 300 nitrosamines have been classified as either a carcinogen or a mutagen. [1], [2]. The affected or specifically the target organs of nitrosamine attack are the lungs and liver. There are no data that suggest it attacks the brain, nor are there data that suggest that nitrosamines are blocked by the placenta barrier. [2], [3].

Another significant aspect of nitrosamine safety can be found in a plant's air quality. Since most nitrosamines are volatile at low temperatures, leeching of nitrosamines into the air of production areas and warehouses poses an unacceptable risk to the safety of employees.

Nitrosamines are formed by the simple and quick reaction of amines and nitrosating agents. While some of these combinations of amines and nitrosating agents are added to achieve a desired effect, some of these chemicals occur naturally. They are commonly used in the following industries: Chemical, Cosmetic, Food, Leather, Metal, and Rubber. Therefore, non-rubber products and production plants that are known to produce nitrosamines include: beer, canned fish, cured meats, pesticides, shampoo and tanneries. Rubber articles that tend to generate (or have generated) nitrosamines due to the use of nitrosamine generating accelerators (dithiocarbamates, sulfenamides, thiurams, sulphur donors or chemicals containing secondary amines) include athletic shoe soles, baby bottle nipples, condoms, gloves, milking inflations, pacifiers, pharmaceutical items (stoppers, plunger seals, *etc.*), radiator hoses, sealing systems, tires and windshield washer tubing, to name a few.

The purpose of this paper is to provide options for the production of rubber products, with a review of compounding alternatives that either reduce or eliminate the production of nitrosamines.

II. NITROSAMINE

Nitrosamines are compounds of the chemical form R_1NNOR_2 (see figure 1 for chemical structure). They are produced by the reaction of nitrite with secondary amines (Mirvish, 1995). While many nitrosamines are carcinogenic, some are not, and their potency varies depending on their molecular structure (Dai, 1998; Luan et al., 2005). N-nitrosodimethylamine (NDMA), a highly potent carcinogen, is commonly detected and often used as an indicator compound for nitrosamines. The degree of carcinogenicity among these compounds varies dramatically. N- Nitrosodiethylamine (NDEA) is the most potent carcinogen among the nitrosamines, and N-nitrosodiphenylamine (NDP (h) A) being 15,000 times less potent. (European Commission, 2007).

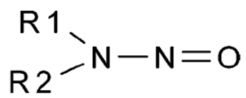

Fig. 1: Structure of nitrosamines. From Luan et al., 2005

The main compounds investigated by health and regulatory authorities have been NDMA (Figure 2) and NDEA. The United States Environmental Protection Agency (EPA) has also developed an analytical measurement method covering seven nitrosamines, which are listed in Table 1 (Munch and Bassett, 2004). Following policy activities in national and international settings, this report will focus on regulations and supporting analyses produced for NDMA and NDEA, and will reference other nitrosamines, as appropriate and where information is available. It is important to note, however, that the use of a highly-potent carcinogen as an indicator could lead to overestimating nitrosamine risks (European Commission, 2007).

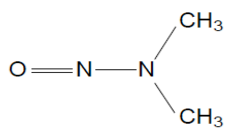

Fig. 2: Structure of N- nitrosodimethylamine (NDMA)

Nitrosamine Analyte	Chemical Abstract Services (CAS) Registry Number	Detection Limit for EPA Method 521 (ng/L)
N-Nitrosodimethylamine (NDMA)	62-75-9	0.28
N-Nitrosomethylethylamine (NMEA)	10595-95-6	0.28
N-Nitrosodiethylamine (NDEA)	55-18-5	0.26
N-Nitrosodi-n-propylamine (NDPA)	621-64-7	0.32

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N-Nitrosodi-n-butylamine (NDBA)	924-16-3	0.36
N-Nitrosopyrollidine (NPYR)	930-55-2	0.35
N-Nitrosopiperidine (NPIP)	100-75-4	0.66

Table. 1: Nitrosamines covered by EPA Method 521

III. NITROSAMINE (NA) CHEMISTRY

To understand NA formation, a brief explanation of amine chemistry is required. Amines are chemical compounds derived from ammonia (NH_3). By substituting one or all the hydrogen (H) in ammonia with a carbon-containing group (-R), primary, secondary and tertiary amines are created. The substitution of one hydrogen atom with one carbon containing group produces a primary amine. The substitution of two or three hydrogen atoms with two of three carbon-containing groups produces secondary and tertiary amines, respectively.

NH_3	RNH_2	R_2NH	R_3N
Ammonia	Primary Amine	Secondary Amine	Tertiary Amine

Table. 2: Amines Types

NITROSATION

NAs are formed by secondary amines reacting with oxides of nitrogen. Very common accelerators such as dithiocarbamates, sulphenamides and thiurams break down and produce secondary amines. Oxides of nitrogen are formed by heating any compound containing nitrogen, even air (atmospheric oxides). This reaction is called nitrosation.

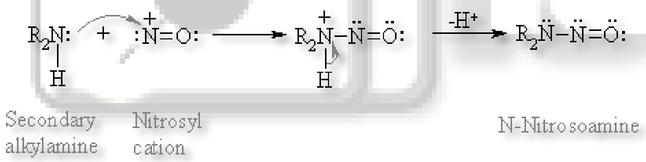

Fig. 3: Nitrosation Reaction

There are four classes of common rubber accelerators that during the curing process form reactive intermediate structures that contain secondary amines. If the sentermediates react with nitrosating agents, nitrosamines can be formed. These four classes of rubber accelerators are:

- Dithiocarbamates
- Sulfenamides
- Sulphur Donors
- Thiurams

A. DITHIOCARBAMATE:

The dithiocarbamates are secondary accelerators that are used at low phr levels in a rubber compound to "tweak" the cure system to a desired rate of cure. Examples of dithiocarbamates include ZDBC, ZDMC, ZEPC, Z5MC, SDMC, LDMC, NDBC, BDMC, CDMC, ZDEC, TDEC, *etc.* Almost every dithiocarbamate has the ability to form a regulated nitrosamine in the presence of a nitrosating agent.

B. SULFENAMIDES:

The sulfenamides are primary accelerators that are used at low phr levels in a rubber com- pound and can influence not only the rate of cure, but also the scorch safety of the compound. Due to this nature, the sulfenamides have been termed fast-delayed action accelerators. A feature of the sulfenamides is that three of them are based on morpholine and can generate the regulated nitroso-morpholine. They are MBSS, OBTS and OTOS (Cure-Rite® 18). However, there are three sulfenamides that do not produce regulated nitrosamines. These include CBS, DCBS and TBBS.

C. SULFUR DONARS:

Sulphur donors are accelerators that are used in a rubber formulation when improvements in heat aging and compression set are required. They are unique in that they provide either mono or disulfidic bonds to the rubber compound. Unfortunately, the most common sulphur donor, DTDM, is based on morpholine, and just like the three sulfenamides, produces a regulated nitrosamine.

D. THIURAMS:

The thiurams are secondary accelerators used in a rubber formulation at low phr levels to "tweak" the cure system to a desired rate of cure. Although the thiurams are not as fast as the dithiocarbamates, thiurams act as both an accelerator and as a sulphur donor. Examples of common thiurams include DPTT, TBTB, TETD, TMTD, and TMTM.

IV. ACCELERATOR CLASSIFICATIONS

Based on the various functional groups of the accelerators they are classified in the above table as Low (safe) or No Nitrosamine producing accelerators to replace the conventional Nitrosamine producing accelerators.

Chemical Family	Safe NAs	No NAs	Replace
Sulphenamides	DCBS	CBTS, BBTS	OBTS, OMTS, MBSS, OTOS
Thiazoles		MBT, MBTS, ZMBT	
Guanidines		DPG, DOTG	
Thiurams	TBzTD, IBT[1], IBM[1]		TETD, TMTM, TMTD, DPTT, TBTD
Dithiocarbamates	SAA-30, Arbestab Z ZBED		MZ, EZ, BZ, CuDD, ZPD, TDEC, BiDD
Non-Nitrogen		AS-100, ZIX, VS	DTDM

[1] very low levels of NAs

Table. 3: Accelerator types

V. CONCLUSION

Germany leads the world in legislation and the elimination of nitrosamines in the work place. In its "Technical Rules for Dangerous Substances" (TRGS 522), eight suspected carcinogenic nitrosamines are listed that are commonly used in cure systems by the rubber industry. Additionally, the TRGS 522 sets the following restrictions;

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- 2.5 (g/m^3) for vulcanization / following production steps / warehousing of technical rubber goods.
- 1.0 (g/m^3) for production steps before vulcanization and warehouses.

Slowly, the United States and Canada are beginning to regulate nitrosamines. Two of the “Big Three” companies have set Engineering Specifications limiting or liminating, their use in automotive rubber parts. Both have published specifications that require a supplier to list the level of nitrosamines present in the rubber parts.

Considering the above facts rubber technologist will require more and more tools in future to meet the stringent environmental and health risk related guidelines. This review of accelerator systems will provide insights of Nitrosamine formation and possible alternative to conventional rubber curing systems.

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