Nitrosamine Solutions

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Nitrosamines (NAs) are a family of chemical compounds discovered over 100 years ago. It was not until the 1950s that these compounds received worldwide attention. In the 1950s, British scientists, Barnes and Magee et al., discovered that dimethylnitrosamine was a powerful carcinogen in experimental animals. This finding led to massive studies involving NAs in many industries throughout the years. Due to the advent of more reliable, sophisticated testing equipment developed in the early 1980s, over 250 different nitrosamine (NA) compounds have tested positive as mutagens (chemicals that change DNA) and carcinogens. NA compounds tend to target organs such as the liver, kidney, lungs, skin and eyes.

Industries in which NAs are typically found are: Rubber, Food, Metal, Leather and Chemical. Products and manufacturing facilities common to NA development are: tobacco, cured meats, beer, pesticides, tanneries and rubber articles that are vulcanised with very common, traditional accelerators. Particular rubber parts with NA concerns are baby teats (nipples) and soothers (pacifiers), potable water components, pharmaceutical articles, condoms and gloves. Also, and just as important, any rubber facility's air quality is of major NA concern for the safety of the workers when utilising accelerators that produce NAs.

The focus of this booklet will be NAs in the Rubber Industry with major emphasis on dry rubber compounding techniques. This literature discusses the chemistry and formation of NAs, current regulations, cure systems contributing to the formation of NAs and alternative cure systems and additives to reduce, inhibit or eliminate NAs in rubber products.

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 hydrogens (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

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:

Secondary Amine　　Nitrogen Oxides　　Nitrosamine (NA)

As stated above, secondary amines (R_2-NH) are of most concern. Primary amines (R_1-NH_2) do form NAs, but they are very unstable and quickly decompose. Tertiary amines (R_3-N) typically do not form NAs. For these reasons, secondary amines have been extensively investigated by the FDA and BGA (Germany). These agencies have found that most secondary amines produce harmful or "regulated" NAs. Some secondary amines do produce "safe" or non-regulated NAs. Further discussion on these NAs will follow.

NAs are produced mostly during the curing and post-curing process of rubber components. Therefore the air quality leading to exposure of NAs to workers in manufacturing facilities is very important. In addition, NAs migrate to the surface on rubber parts after cure during storage and use. Some major tyre companies have detected substantial NAs levels in tyre warehouses and have installed ventilation equipment in these facilities. Primary routes of exposure are ingestion, inhalation and dermal (skin) contact. All types of potential exposures have been and will be further addressed by regulatory agencies.

REGULATIONS:

After levels of over 300 ppb (parts per billion) of NAs were discovered in baby teats and soothers, many countries set maximum permitted NA levels on these products:

Country	***Nitrosamines ppb max.[1]***	***Nitrosatables ppb max.***
Australia	20	400
Denmark	5	100
Netherlands	1	100
Canada	10 each – 60 total	nr
Switzerland	10	200
Germany	10	200
UK	10 each – 30 total	100
USA	10 each - 60 total	nr

[1]extractions in artificial saliva or dichloromethane (US, Canada), nr-not regulated

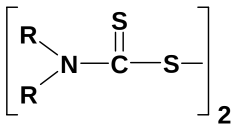
Currently in Germany, workplace atmospheric concentration of NAs are regulated at $1 ug/m^3$. In the US and Canada, workplace atmospheric concentration of NAs are not regulated to date. Agencies and unions in the US and Canada and other countries are monitoring, documenting and reporting NA levels in rubber facilities to petition their governments for restrictive limits. Interesting to note that the German regulation ($1 ug/m^3$) now includes the cabin space of automotive vehicles. This is causing automotive suppliers, especially window and door sealant manufactures, to reformulate compounds with accelerators that do not produce regulated NAs. In the future baby teats and soothers' NA regulations will be implemented to include toy balloons, condoms and possibly pharmaceutical articles. Even warehouse facilities of cured elastomer articles are being investigated for NA levels.

Detection of NAs is relatively easy with the use of some sophisticated analytical equipment. High Performance Liquid Chromatography (HPLC), Gas Chromatography (GC), Mass Spectroscopy (MS) and Thermal Energy Analyzer (TEA) can detect NAs as low as 0.1 ug/kg. The equipment listed can also determine different types of NAs, "safe" and "regulated" NAs.

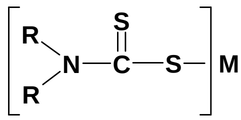
ACCELERATORS WITH REGULATED NAs

Unfortunately, the most utilised families of accelerators incorporated into cure systems for elastomers produce "regulated" or harmful nitrosamines. These families include: Dithiocarbamates, Sulphenamides, Thiurams and some sulphur donors. Again, these chemistries or chemical compounds break down and form secondary amines that are nitrosatable by oxides of nitrogen.

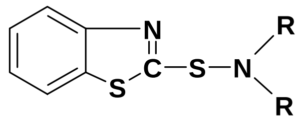
Thiurams



Dithiocarbamates



Sulphenamides



Thiurams are secondary accelerators or "kickers" used at very small quantities to fine-tune the cure system. All the most commonly utilised thiurams are secondary amines that readily form regulated NAs. These include: TMTM, TMTD, TETD, TBTD and DPTT.

Dithiocarbamates, like thiurams, are secondary accelerators used at very small quantities to fine-tune the cure system. These kickers are slightly faster and more active than the thiurams. Also, dithiocarbamates are extensively used in latex cure systems. All the major accelerators in this group produce regulated nitrosamines including: MZ (ZMDC), EZ (ZEDC), BZ (ZBDC), ZPD, TDEC, CuDD and BiDD.

Sulphenamides are delayed-reaction primary accelerators used extensively to produce scorch safety and fast cure rates. When considering NAs in an elastomeric formulation, the selection of sulphenamides is a little more forgiving than the chemistries above. About half of the industrial important sulphenamides do not produce regulated NAs: BBTS (TBBS), CBTS (CBS) and DCBS. The other half, OBTS, MBSS and OTOS (Cure-Rite®18) are based on morpholine and produce the regulated nitrosamine nitroso-morpholine. This nitrosamine derivative is considered one of the most potent NA carcinogens tested in laboratory animals.

Another commonly used accelerator that generates a harmful nitrosamine is Accelerator R (DTDM). This accelerator is also based on morpholine. It is selected as a powerful sulphur donor to create mono- and di-sulphur crosslinks to improve the heat aging and compression set resistance characteristics of rubber compounds. Other accelerators that produce regulated NAs are: amines (HEXA), aldehyde amines and thioureas (ETU, DETU, etc.). Fortunately, Robinson Brothers has a full line of accelerators, some traditional and some new chemistry, to offer that do not produce regulated NAs or any type of amine. The latter are compounds that do not contain any nitrogen, thus eliminating the NA issue completely.

SOLUTIONS TO THE NITROSAMINE ISSUE

To combat the NA issue a compounder has three options or a combination of options:

- Avoid compounds that produce NAs completely
- Use only safe non-regulated NA generating additives
- Use an inhibitor to absorb NAs

In addition to the options above and whether NAs are an issue or not, proper environmental measures must be practiced. Education and training of all employees, general good manufacturing practices, the use of fresh air ventilation and proper respirators and protective clothing are essential to any manufacturing process. These controls may not eliminate NAs, but will greatly reduce the exposure of NAs to employees, especially in curing and post-curing operations. Within the cured product, NAs are still available to migrate during storage, in operation and/or be extracted. Also, it should be mentioned that factory processes, i.e., salt bath curing when using nitrogen-containing salts could produce harmful NAs. First lets consider accelerators that do not produce any NAs.

Non-Nitrogen Containing Accelerators:

Xanthogens (AS-100, ZIX), phosphates (Accelerator VS), peroxides and resin cures are products of non-nitrogen containing curatives. Peroxides and resin cures are certainly viable options if the function of the part and physical properties permit. Not all elastomers can be resin or peroxide cured. Resin cures are utilised in niche situations where certain properties are required (steam resistance – butyl curing bags). Peroxide cures are typically used in situations where excellent compression set and heat resistance are required. Peroxide cured products can be difficult to process and have limited physical properties. The use of peroxide curatives is growing every year, but sulphur/accelerator systems still dominate the rubber industry.

Accelerator VS is an interesting, traditional option. This is a zinc salt of dibutyl phosphorodithioate (liquid) on a silica carrier (62% active solid). It does not contain any nitrogen and therefore cannot generate NAs. Accelerator VS is typically used in EPDM and NR compounds. This accelerator tends to be scorchy, but certainly a viable alternative.

Accelerator ZIX is a very fast accelerator and chemically known as zinc iso-propylxanthate. Due to its very scorchy nature, this accelerator has a very limited, but important use in the rubber formulations. Typically, ZIX is used in very low or room temperature cure systems for adhesive cements, tank linings, coatings, patching compounds, etc.

Robac®AS-100 is a new alternative, primary accelerator used globally in dry elastomers and latex. This compound is diisopropyl xanthogen polysulphide, which does not contain any nitrogen, phosphorus or metallic components and donates about 10% sulphur. AS-100 has FDA approval per FDA 21 CFR. 177.2600 and has been selected as the primary or secondary accelerator of choice in such rubber articles as: baby soothers and teats, balloons, condoms, gloves, black filled NR, IR and NBR vulcanizates. Other interesting characteristics of AS-100 are: completely consumed during cure, highly soluble in rubbers (non-blooming), free from copper staining and taste and easily dispersible. Below is data pertaining to a sulphurless cure systems utilising AS-100:

Cure System	***TS_2 mins.***	***T_{50} mins.***	***T_{90} mins.***	***MH lb-in***	***Hardness pts.***	***Mod. 500% psi***	***TS psi***	***EB %***
TMTD	1.37	3.26	7.28	45.0	48	1204	3422	700
AS-100	1.46	2.34	4.52	27.4	30	493	2132	890
TB_zTD/AS-100	2.00	3.27	6.21	39.0	43	798	3089	890

Compound: SMR CV-100, ZnO-5, S.Acid - 1, AO-1, N762-5, $CaCO_3$-50, Accelerator-3. Cure: 160C/T_{95}

AS-100's rheological data shows that it's marginally less scorchy, but considerably faster than TMTD. The state of cure of the compound utilising AS-100 is lower than TMTD. This is easily corrected by the addition of Accelerator TBzTD (thiuram, safe nitrosamine generator) working synergistically with AS-100. Accelerator AS-100 also works well in combination with sulphenamides to produce low compression set, sulphurless EV cure systems.

Cure System	***Hard. pts.***	***Mod. 300% psi***	***TS psi***	***EB %***	***Comp.Set 24hr/70C, %***	***Comp.Set 24hr/100C, %***	***NAs ug/kg***
A - traditional	56	1494	3234	509	9	15	~ 200
B - safer	54	1378	3219	529	10	15	ND
Heat aging A	+ 1	- 15	- 25	- 5	--	--	--
Heat aging B	+ 3	- 2	- 17	- 5	--	--	--

Compound: SMR CV-100, ZnO-5, S.Acid-2, AO-1.0, N550-45, $CaCO_3$-50, Paraffinic oil-4, Wax-3, AOz-3, Accelerator-3.
Cure Systems: A-Accelerator R-1.0, OBTS-1.0, TMTD-1.0. B-AS-100-1.2, TB_zTD-2.2, BBTS-1.0
Cure: 160C/T95, Heat Aging: 168 hrs./100C, ND – none detected

The data reflects that AS-100 used in combination with TB_zTD and BBTS can create a compound very close to the performance of the traditional Accelerator R, OBTS and TMTD system used for low compression set and good heat aging. The obvious benefit to the AS-100 cure system is the low levels of NAs. BBTS and TB_zTD both produce NAs, but of the non-regulatory type. In contrast, Accelerator R and OBTS produce N-nitroso-morpholine and TMTD produces N-nitrosodimethylamine, both regulated NAs.

Non-Regulated or Safe NA Producing Accelerators:

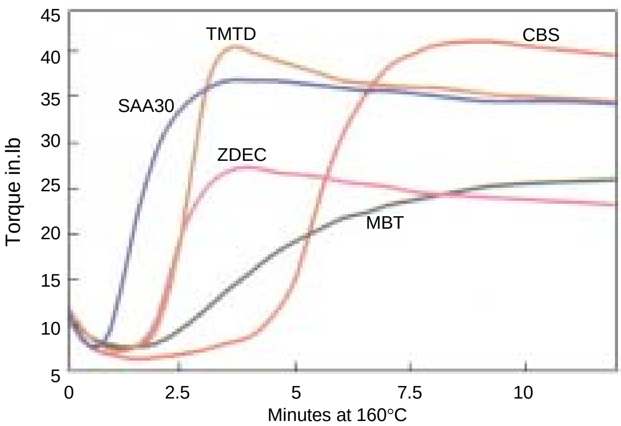
Below is a listing of accelerators that produce non-regulated, "safe" NAs or cannot produce any type of NAs because they do not contain secondary amines or any nitrogen:

Chemical Family	***Safe NAs***	***No NAs***	***Replace***
Sulphenamides	DCBS	CBTS, BBTS	OBTS, OMTS, MBSS, OTOS
Thiazoles		MBT, MBTS, ZMBT	
Guanidines		DPG, DOTG	
Thiurams	TB_ZTD, 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

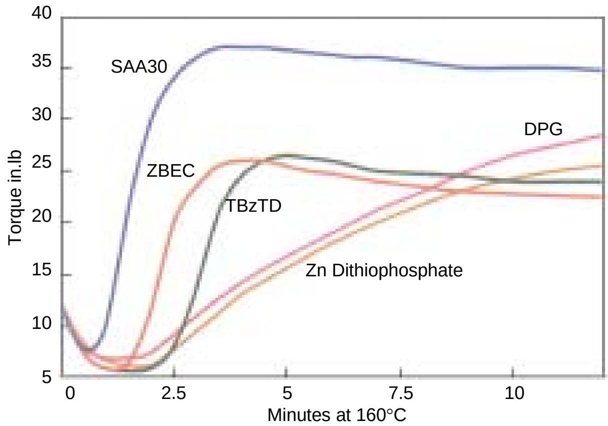
[1] very low levels of NAs

There is a lot of literature published concerning the more traditional accelerators like MBT, MBTS, CBTS, BBTS, DPG, etc. Therefore, lets focus on some interesting, non-traditional, safe NAs generating accelerators such as: Robac® SAA-30, Cure-Rite® IBM, Cure-Rite® IBT and ZBED.

Robac® SAA-30 PM 50 is a new, interesting, ultra fast accelerator chemically know as 2,2' – dithiodi(ethylammonium) – bis (dibenzyldithiocarbamate). This product is available as a 50% rubber-bound dispersion in cylindrical pellet form. SAA-30 functions as a secondary accelerator, which can replace conventional dithiocarbamates (MZ, EZ, BZ, etc.) and thiurams (TMTM, TMTD, etc.). Below are some results utilising SAA-30 as a secondary accelerator:



SAA-30 vs. other classes of accelerators



SAA-30 vs. "safe" NAs generators

The rheologies above show the cure characteristics of SAA-30 in the following test compound: SMR CV-100 phr, zinc oxide-5, stearic acid-1, antioxidant-1, N762 carbon black-5, calcium carbonate-50, sulphur-1.2, and accelerator-0.5. This accelerator produces fast cures, i.e. short scorch and rate of cure. The state of cure in most cases is comparable to thiurams. Also, note when compared to other safe NA generating accelerators, SAA-30 produces a fast cure rate with the highest state of cure. SAA-30 in natural rubber produces some very interesting and favorable physical, ageing and dynamic properties when compared to other traditional dithiocarbamates.

Cure System	*Hard. pts.*	*TS psi*	*EB %*	*Hard.[1] pts.*	*TS[1] psi*	*EB[1] %*	*Fatigue[2] cycles x 100*
EZ	44	3248	840	35	2393	680	509
SAA-30	50	3698	780	50	3205	680	1039
ZBED	37	2146	980	32	1900	830	836

Compound: SMR CV-100 phr, ZnO-5, S.Acid-1, AO-1, N762 carbon black-5, $CaCO_3$-50, sulphur-2.5, accel.-0.6.
[1] heat aged: 168 hrs./70C, [2] fatigue to failure: JIS ave. 100% extension.

When SAA-30 is used as a primary acceleratory and compared to accelerator EZ (table above), SAA-30 produces higher initial properties and superior heat aged and dynamic performance. SAA-30's values also outperform the safe generating NAs accelerator ZBED.

Cure System	*Hard. pts.*	*TS psi*	*EB %*	*Hard.[1] pts.*	*TS[1] psi*	*EB[1] %*	*Fatigue[2] cycles x 100*
TMTD/CBTS	55	3843	630	55	2378	470	792
SAA-30/CBTS	56	3698	620	55	2552	480	840

Compound: SMR CV-100 phr, ZnO-5, S.Acid-1, AO-1, c.black-5, $CaCO_3$-50, sulphur-1.25, CBTS-1.6, TMTD/SAA-30-0.3.
[1] heat aged: 70 hrs./100C, [2] fatigue to failure: JIS ave. 100% extension.

Very comparable results were obtained substituting SAA-30 for TMTD as the secondary accelerator in the above natural rubber test formulation. Again, the heat aged and dynamic properties are favorable utilising the SAA-30.

Cure-Rite®IBM and Cure-Rite®IBT are non-staining ultra accelerators that produce approximately 100 times less regulated NAs than common thiurams like TMTM and TMTD. IBM is a mono-sulphide thiuram and IBT is a di-sulphide thiuram. Although, IBM and IBT were developed to replace TMTM and TMTD, respectively, both have found applications to replace DPTT, TETD and the pricey TB_ZTD. Two additional characteristics have been discovered with the use of these accelerators. First, both IBM and IBT provided much more scorch safety and shorter cure times than TMTM and TMTD. In fact, in certain formulations, IBM provided increased scorch safety beyond that of a sulphenamide (delayed-reaction accelerator) used alone. Second, both accelerators deliver much less reversion in natural rubber compounds than comparable accelerators. The increased scorch resistance and cure rate combined with reduced reversion translates to shorter cure cycles or increased safety of hard-to-process compounds.

Being a higher molecular weight accelerator, more IBM by weight should be used if replacing other thiurams (1.6 x TMTD phr; 1.85 x TMTM; 1.33x TETD). The exception is the replacement of TBzTD would require only 0.70 as much IBM. IBT also is a higher molecular weight accelerator, therefore a good starting point to replace other thiurams should be (1.7 x TMTD phr; 2.0 x TMTM; 1.4 x TETD). The exception is the replacement of TBzTD which would require only 0.75 as much IBT.

Accelerator ZBED is a popular choice to replace other dithiocarbamates to lower or eliminate regulated NAs levels. This ultra accelerator is chemically, zinc dibenzyl dithiocarbamate. It acts like a typical dithiocarbamate secondary accelerator by decreasing scorch times and cure rate while increasing cure states. ZBED does produce the non-regulated N-nitrosodibenzylamine and is used effectively with sulphenamides, thiazoles and thiurams. ZBED has a high molecular weight relative to other more common dithiocarbamates like MZ, EZ and BZ; therefore about 1.5 times more ZBED is needed to replace common dithiocarbamates. Typical cure systems using ZBED to obtain low NAs levels are:

NR or SBR		***EPDM***		***BUTYL***	
Sulphur	2.0 – 2.5	Sulphur	1.5 – 2.0	Sulphur	1.0 – 2.0
ZBED	0.5 – 1.5	ZBED	1.5 – 2.0	ZBED	0.5 – 1.5
BBTS	1.5 – 2.5	MBT	1.5 – 2.0	BBTS	1.0 – 1.5
MBTS	0.5 – 1.5	CBTS	1.0 – 2.5	IBT	0.7 – 1.2

INHIBITORS:

Rubber compounders have incorporated the use of NA inhibitors into formulations, but typically as a last resort and in combination with the accelerators discussed above. It is believed that NA inhibitors disable nitrogen oxides preventing them from reacting with secondary amines. The concern with these inhibitors is that they are not always effective in the eliminating or reducing levels of NAs. Chemicals that have been tested and in some cases found to reduce NA levels are: ascorbic Acid (vitamin C), α-tocopherol (vitamin E), calcium oxide (Akrocal 90) and alkyl phenol formaldehyde resins (Akrochem P-101).

CONCLUSION:

The Nitrosamine issue has been under investigation for many decades. Both US and German environmental and health related government agencies have imposed limitations on the use of substances that create nitrosamines in the Rubber Industry. More countries in the near future will also impose regulations. More notably, these current regulations are being reviewed and will be altered in the future to stricter standards. For example, in Germany the latest regulation permits a maximum atmospheric concentration of regulated NAs of only 1ug/m^3. This amendment includes the cabin space in automobiles. Therefore, automotive suppliers are placing increased interest on the Nitrosamine issue especially in door and window seals. This interest will trickle over to non-automotive rubber industries and components. Realistically, NAs are far more potent in rubber factories' atmosphere during curing or post curing of rubber. Currently in the US, unions and special interest groups are placing increasing pressures on the EPA and OSHA to set nitrosamine restrictions, not only in the factories, but also in storage facilities. Robinson Brothers offers rubber manufacturers a variety of safe and non-nitrosamine producing accelerators, as well as some nitrosamine inhibitors. Further details and information are available from Robinson Brothers Ltd. Please contact your Technical Salesperson or the Technical Department at Robinson Brothers.

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