



Is REACh a suitable way towards less toxic propellant formulations?

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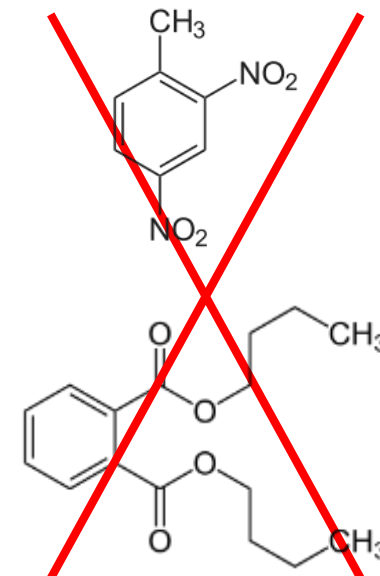
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Introduction – REACH

■ Effects of European REACH Regulation

- ▶ REACH = Registration, Evaluation, Authorisation and Restriction of Chemicals
- ▶ **Dinitrotoluene DNT + Phthalate Esters DBP, DEHP, DIBP are on REACH-list of substances of very high concern**
- ▶ They are banned by European legislation from 2015 !
- ▶ It will be no longer allowed to produce, import or process propellants containing these compounds within the European Community
- ▶ But – most of the propellant formulations used today contain at least one of these components as these formulations originate from the 1950es-1970es
- ▶ These propellants need to be re-designed and re-qualified (including re-qualification of ammunition)



Introduction – REACH

■ Does it make sense to ban these plasticizers from propellants?

■ Certainly for DNT !

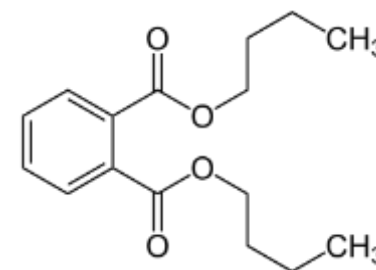
- ▶ Since DNT is really highly toxic / carcinogenic !

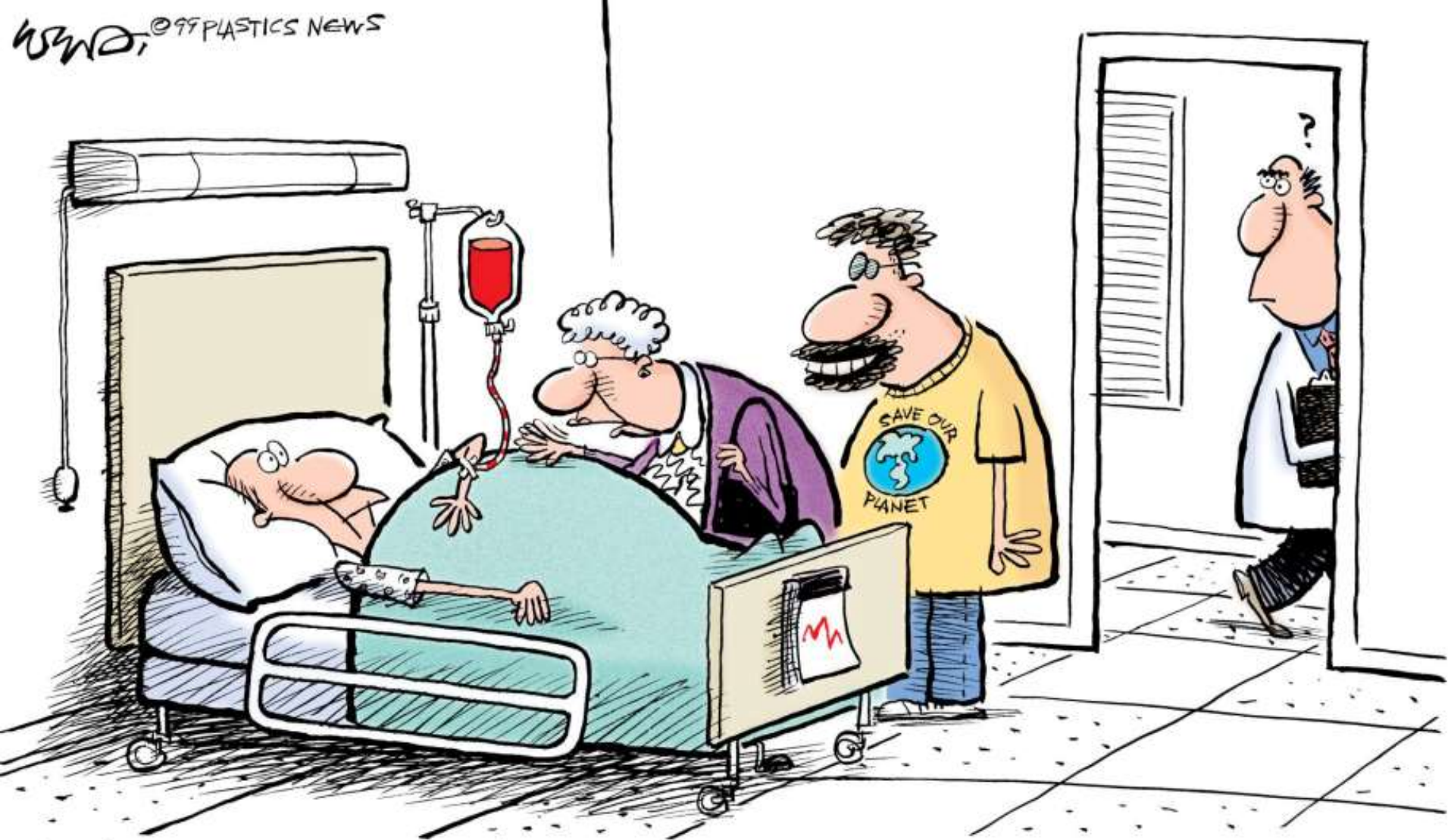
TD 50 = 7 mg/kg/d for 2,6-DNT
TD 50 = 40 mg/kg/d for 2,4-DNT



■ Questionable for phthalate esters

- ▶ Even the banned phthalate esters DBP, DEHP, DIBP show only intermediate human toxicity
- ▶ Main reason for banning them is the huge amount of production and excessive use in consumer products
- ▶ Until recently, cosmetics and personal care products did contain large amounts of phthalates (e.g. shampoos up to 1% and perfumes up to 5%)
- ▶ REACH ban excludes medical applications of phthalates
- ▶ Total amount of phthalates used in propellants is negligible; phthalates are fully burned when the ammunition is fired !



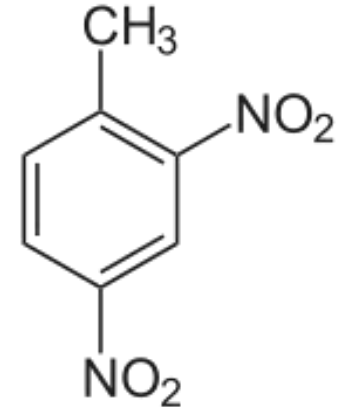


"WE'RE GOING TO ASK THE DOCTORS TO DISCONNECT YOUR LIFE SUPPORT, HOWARD. WE CERTAINLY DON'T WANT YOU ABSORBING ANY PHTHALATES..."

How to replace DNT ?

■ DNT is an excellent plasticizer for propellants

- ▶ Good plasticization of NC
- ▶ Energetic (almost no loss in performance by plasticizer)
- ▶ Cheap
- ▶ Used in large proportions (up to 12%)



■ No suitable replacement available

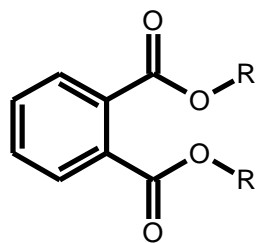
- ▶ TEGDN (Triethyleneglycol Dinitrate) and Butyl-NENA (Butyl Nitrate-ethyl Nitramine) would have similar thermodynamic properties but are more expensive and have much higher migration tendency

■ Possible way to replace DNT

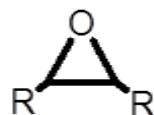
- ▶ Choose a slightly more energetic base formulation (nitrocellulose blend with higher nitrogen / energy content)
- ▶ Add a non-energetic REACh-compatible plasticizer
- ▶ Correct grain web size for changed burning rate

How to replace Phthalate Plasticizers ?

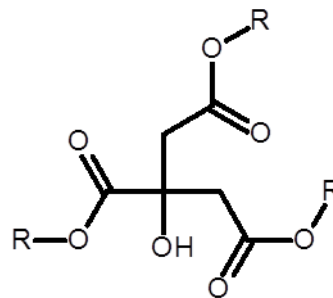
- **If Phthalates have been used in base grain propellant formulations**
 - ▶ Replacement by non-energetic REACh-compatible plasticizer
- **If Phthalates have been used as deterrent / surface coating**
 - ▶ Might be more difficult since the replacement needs to match ballistics
- **Possible replacements are:**



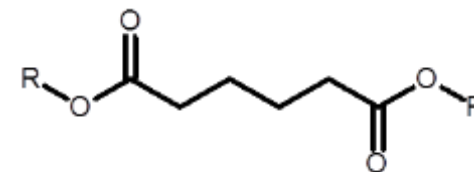
Other Phthalate esters
(with longer side-chain R)



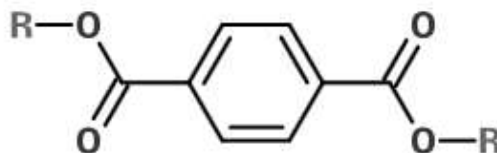
Epoxy esters



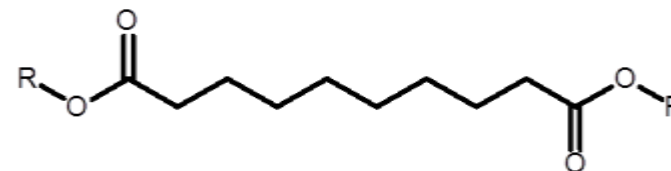
Citric acid esters



Adipate esters



Terephthalate esters



Sebacate esters

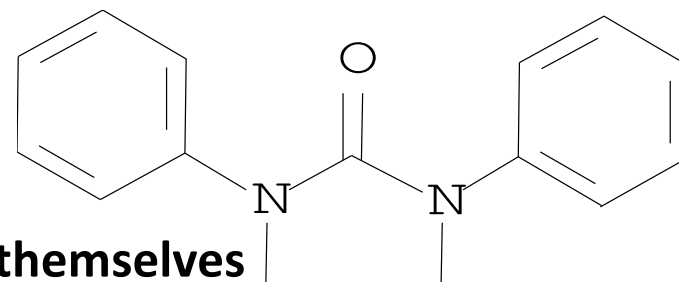
Why not using Centralites ?

■ Centralites have been used in propellants for decades

- ▶ Centralites (Dialky Diphenyl Urea) work as stabilizer and plasticizer
- ▶ Also for surface coating of propellants
- ▶ Centralites are relatively cheap

■ Centralites are not banned by REACH

- ▶ Because Centralites are not very toxic by themselves

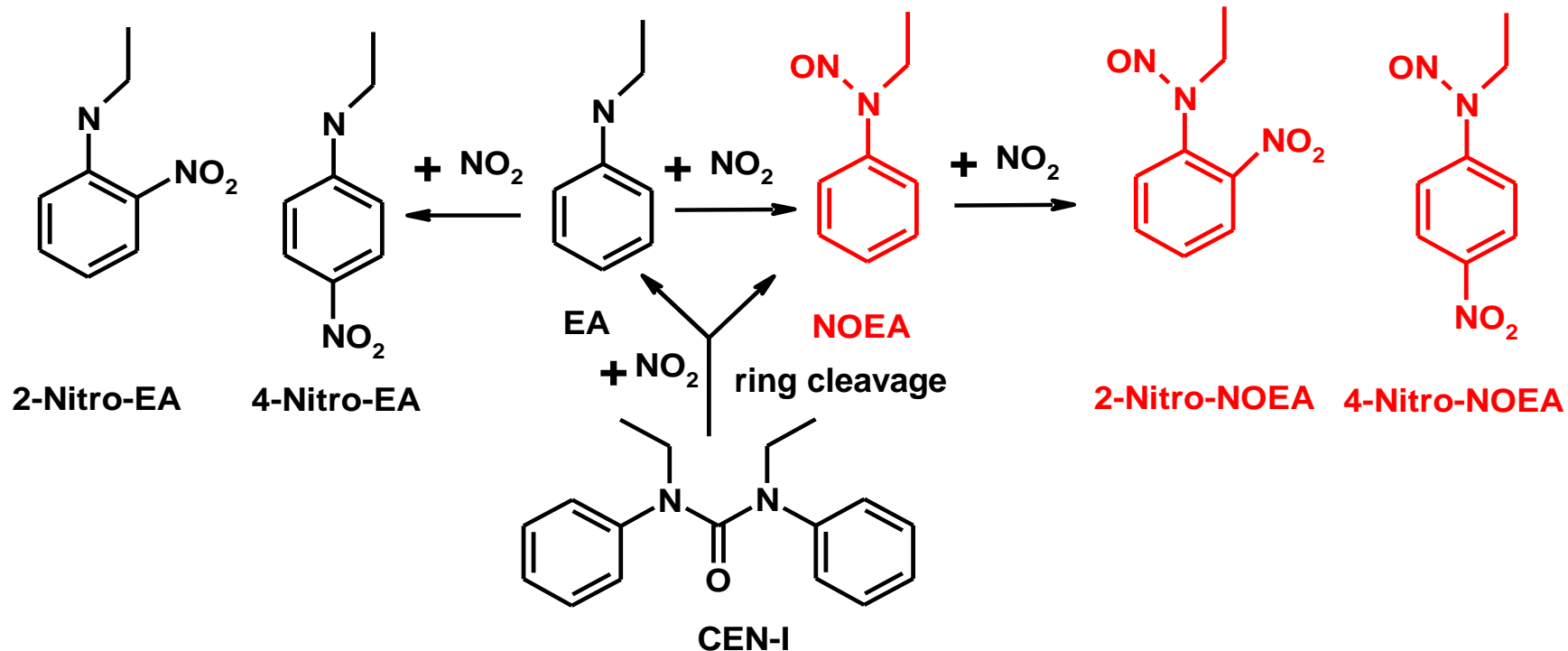


■ But – Centralites are converted into highly carcinogenic products !

- ▶ Centralites are converted into N-Nitroso Alkyl Anilines (NO-AA)
- ▶ NO-AA are extremely toxic / carcinogenic
- ▶ Formulations with $\geq 0.0001\%$ NO-AA need to be declared as carcinogenic
- ▶ NO-AA content in new propellants with Centralites is 0.01 – 0.1% (factor 10 - 100 above declaration limit) and much higher in aged propellants
- ▶ High Centralite concentration in deterred layer accelerates ageing
- ▶ **Therefore, Centralites should no longer be used in propellants !!!**

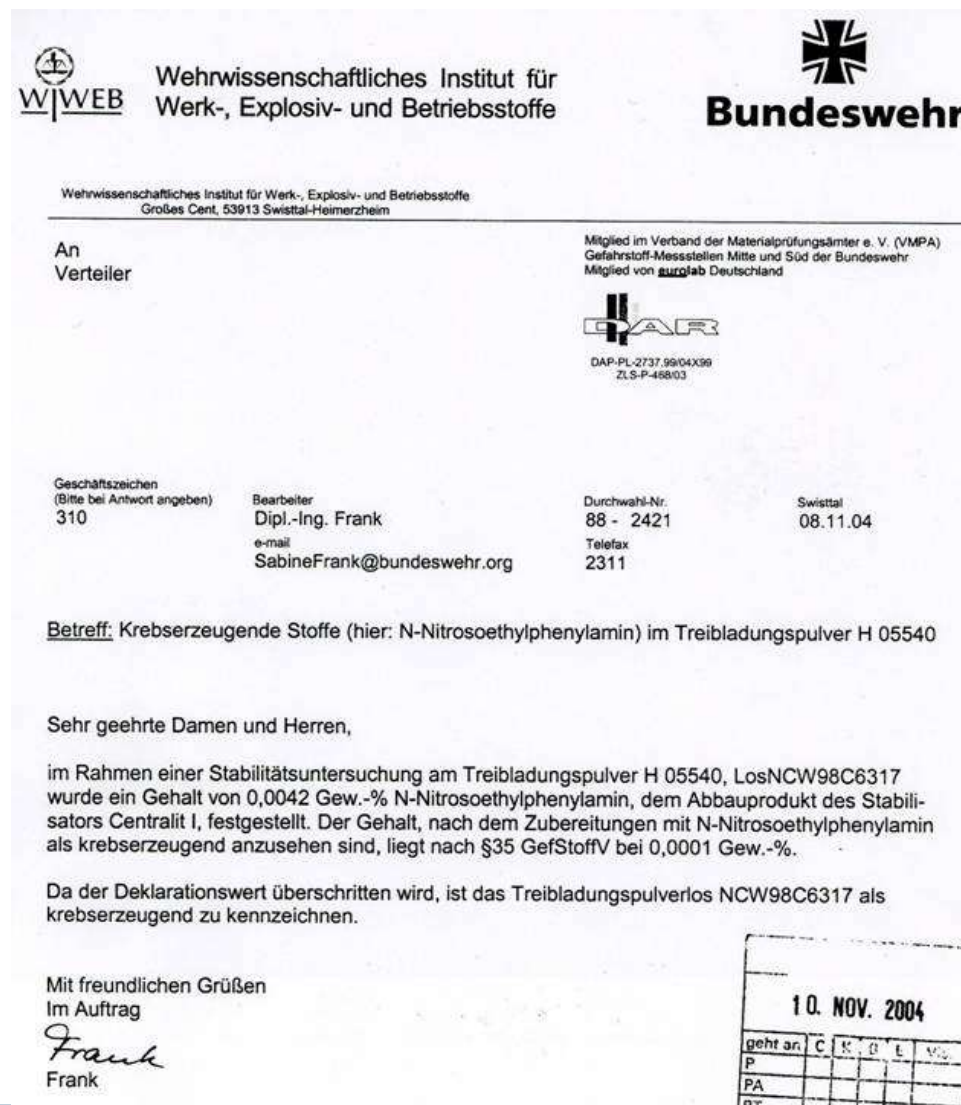
Why not using Centralites ?

- ▶ During propellant production / ageing, Centralites are converted into the extremely toxic / carcinogenic N-Nitroso Alkyl Anilines



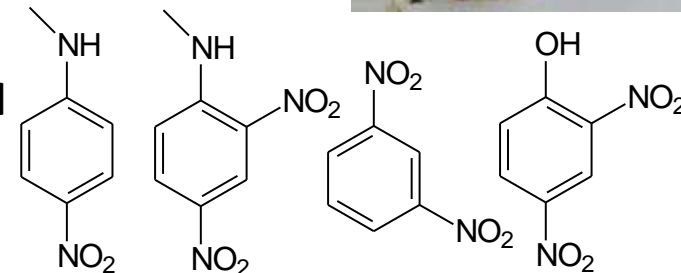
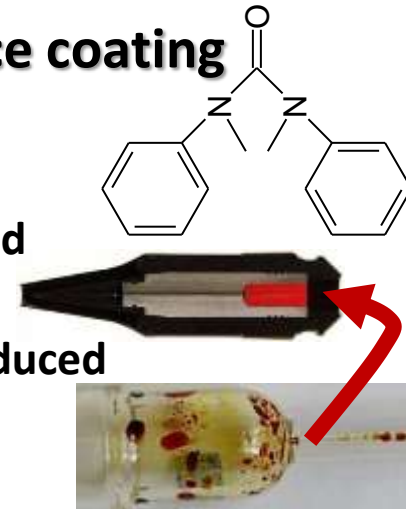
Why not using Centralites ?

- ▶ German MoD consequently implements EU-Directive 1999/45/EC by declaring Centralite-containing propellants as carcinogenic products
- ▶ German MoD strongly recommends to replace Centralite by Akardite-2
- ▶ See e.g. letter of WIWEB Germany from 2004:
.... "since the declaration threshold (for N-nitroso-ethylaniline) is exceeded, the propellant xxx has to be declared as carcinogenic"

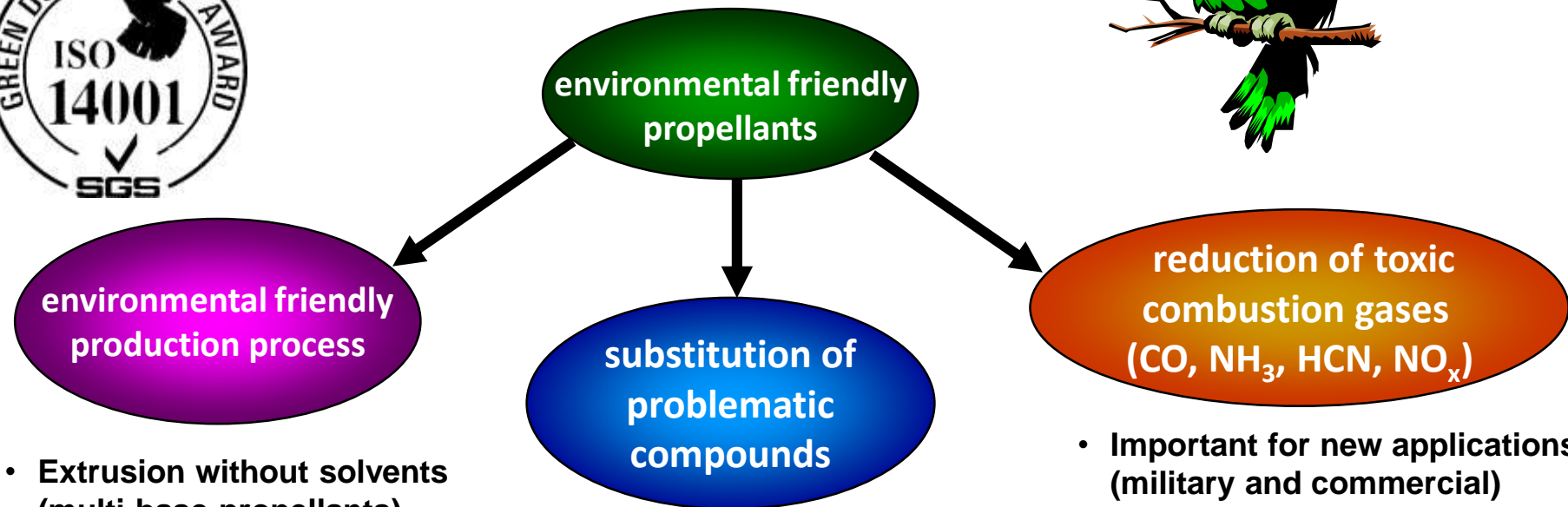


Why not using Centralites ?

- **Surface coating with Centralites accelerates propellant ageing !**
 - ▶ Centralite concentration in deterred region is around 20%
 - ▶ Centralites are not fully compatible with NC / NG → accelerated ageing in the deterred region → **more carcinogenic N-Nitroso Alkyl Anilines**
- **Results of single base propellant with Centralite surface coating**
 - ▶ For a medium calibre propellant, the commonly used deterrent was replaced by Centralite
 - ▶ Extreme temperature ageing of ammunition showed unexpected swelling of tracer pyrotechnics → failing of tracer function
 - ▶ Investigation showed that additional ageing products were produced
 - ▶ Also seen in high-temperature stability tests by appearance of unusual yellow-brown oily condensate
 - ▶ FTIR- and GC-MS-analysis identified a mixture of toxic aromatic nitro / amino compounds in this oil
 - ▶ This oil had migrated into the tracer, causing the problem



Strategy of Nitrochemie (regarding Toxicity)



- Extrusion without solvents (multi-base propellants)
- New plant with reduced VOC-emission (single base)

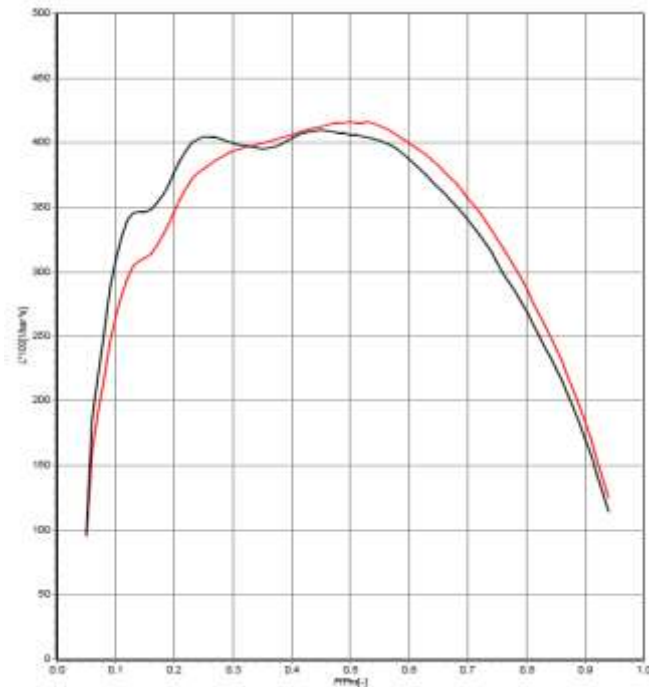
- Goal of Nitrochemie: Substitution of all toxic and problematic compounds in most current and all new propellants and charge systems

- Important for new applications (military and commercial)

Effects of REACh on Nitrochemie Propellants

- **>95% of Nitrochemie propellants are already REACh compatible**
 - ▶ This thanks to the R&D strategy which initiated replacement of toxic components more than 20 years ago
- **6 propellant types are not yet REACh compatible**
 - ▶ Mainly standard US/UK formulations as requested by customers
 - ▶ New REACh compatible formulations are in development (for 1 propellant type) or in qualification (for 3 propellant types)
 - ▶ Remaining propellant types have not been produced for some time, REACh compatible formulations will be implemented with next order
- **Gained experience with formulation change**
 - ▶ In some formulations, DBP can simply be omitted
 - ▶ In other formulations, DBP can just be replaced by other plasticizers
 - ▶ Replacement of DBP as surface coating agent can be more difficult
 - ▶ Even 5% DBP + 10% DNT in artillery propellants can easily be replaced

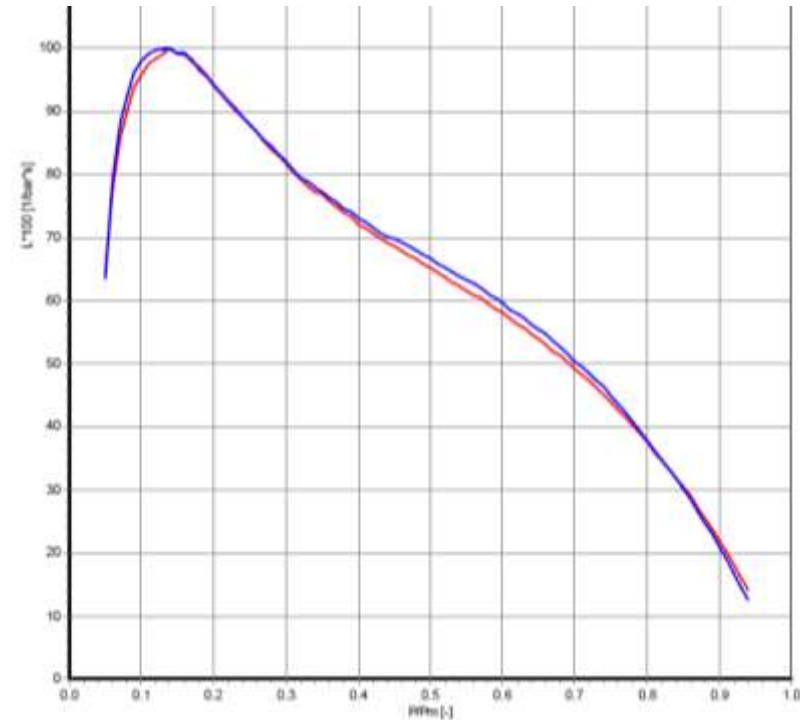
Nitrochemie Propellants – Examples



Porous propellant:

Red: Original propellant with DBP

Black: Replacement propellant without any plasticizer



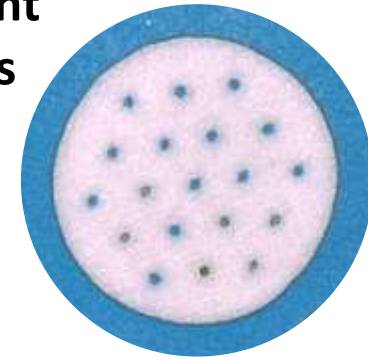
Ignitor propellant:

Red: Original propellant with DBP

Blue: Replacement propellant with non-toxic plasticizer

Nitrochemie Propellants – Examples

- Development of a 19-perforated REACH-compatible propellant suited for 76mm standard and high performance applications
- 76mm "standard" rounds: TP, Spotter, HE and HE-PFF
 - ▶ $V_0 = 915$ m/s at projectile weight 6.3 kg
 - ▶ Replacement of toxic / sensitive propellant OD6230 (contains DNT / DBP / DPA) by non-toxic REACH-compatible ECL[®] formulation
 - ▶ Qualified / introduced in Germany
- 76mm round with steerable sub-calibre projectile for DAVIDE anti-missile system
 - ▶ $V_0 = 1'180$ m/s achieved (projectile weight = 4 kg)
 - ▶ In development (Italy)



Partner:

DIEHL



Partner:

 **OTO MELARA**

Summary, Discussion and Conclusions

- **The European REACH Regulation bans DNT and phthalate esters**
 - ▶ This ban causes major problems for European propellant manufacturers
 - ▶ Many propellants need to be re-designed and re-qualified
- **Nitrochemie started replacement of toxic components 20 years ago**
 - ▶ Only a small fraction of propellants (<5%) is not yet REACH compatible
- **At least from one case within Europe it is known that DBP surface coating will be replaced by centralite – although not banned by REACH, centralites produce highly toxic and carcinogenic decay products during propellant ageing**
- **A 12-years extension ("REACH waver") for use of DBP in propellants is likely to be granted by the European Commission since some other propellant manufacturers are unable to replace DBP in their formulations**
- **It is not yet visible whether propellant manufacturers from outside of Europe will follow with replacing DNT and phthalate plasticizers**
- **Therefore, the assumption that REACH will globally lead to a significant reduction in propellant formulation toxicity has to be questioned**

Thanks very much for your attention !

