



Banning of harmful chemicals will play an important role in the plastic industry

The European Commission has confirmed the obligation for Pre-registration by recyclers if they want to keep their business running according to the European law. Deadline is midnight of 30 November 2008. In Europe, chemicals are subjected to REACH that identifies several families of substances according to the proved or assumed toxic and polluting effects, for example:

- CMR: Abbreviation for Carcinogenic, Mutagenic, and Reproductively-toxic. Only those for which there is a high level of evidence of health damage to humans are subject to authorization under REACH.
- PBTs: Substances of very high concern that are persistent, bio-accumulative and toxic. Those substances may become subject to authorization as a priority.
- vPvB: Substances of very high concern that are very persistent, very bio-accumulative. Those substances are subject to authorization.
- POPs: The Stockholm Convention on Persistent Organic Pollutants (POPs) sets out to control the production, use, import, export, disposal and release of twelve POPs. The convention bans deliberate production and use of POPs and the development of new POPs, and aims at minimizing releases of unintentionally produced POPs. The European Community has recently proposed that 5 additional substances should fall under the Convention Endocrine disrupters.

Asbestos is banned because of its own properties. Colorants and pigments can be banned because of their cadmium content superior to a level threshold. Partial ban is the most common.

- Specific regulations can ban a substance for specific applications and its use can be authorized in other applications. Good examples are the food contact polymers where some plasticizers or accelerators are totally or partially banned.
- In a same country some nitrosamines are banned and others are not.
- In different countries, a substance can be banned or not, for example formaldehyde in building insulation.
- A level threshold can limit the use of a given additive, for example several heavy metals.

Certain elements or molecules are not banned but the pressure of public opinion arouses suspicion leading to look to their replacement as a precaution. It is the case for PVC in automobile or medical applications.

Consequences for the polymer industry emerge from two categories:

- Ban of additives: fillers, plasticizers, colorants and pigments, stabilizers etc. and need to use substitutes.
- Ban of processes: for example, degreasing with certain halogenated solvents before painting or joining needing to apply another process or to use substitutes.

The following pollutant list is not exhaustive and products can be partially or totally banned, of limited use or threatened:

- Gases such as carbon dioxide, carbon monoxide, hydrocarbons, nitrogen oxides, sulphur dioxide... On a weight-for-weight basis, the contribution of N_2O to the greenhouse effect is roughly three hundred times greater than that of carbon dioxide. Sulphur dioxide and other sulphur oxides are formed during the incineration of fossil fuels and wastes, contributing to acidification. The reduction of CO_2 emission will affect the polymer industries in the same way as the other activities.
- VOCs or Volatile Organic Compounds form a broad category of volatile chemical compounds, some of which pose a health hazard. The presence of VOCs in the atmosphere can also lead to greenhouse effect, ozone layer depletion and acidification.
- CFCs, HCFCs, HFCs, PFCs and other halogenated gases: halogenated fluorocarbons, perfluorinated carbons, and hydrofluorocarbons. Freons are chlorofluorocarbons (CFCs), whose molecules have one or more hydrogen atoms replaced by halogens (chlorine and/or fluorine). Formerly used as coolants and expanding agents in insulation foam they contribute to the depletion of the ozone layer and an increased greenhouse effect. Their use is now regulated or banned in many countries.

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Heavy metals, including mercury, zinc, copper, cadmium, vanadium and lead, are harmful if spread in the environment.

- Mercury is used in catalysts and is released by the combustion of fossil fuels and wastes. Organic mercury compounds act as cumulative poisons that affect the nervous system.
- Zinc is used as curing activator for rubber and for PVC stabilization.
- Copper is used in pigments for plastics and rubbers.
- Cadmium is a cumulatively toxic element.
- Lead, accumulates in biological systems and is linked to behavioural changes, paralysis and blindness. It was used as curing activator or stabilizer for certain polymers.
- Some plasticizers, fire retardants, curing agents..such as:
 - Chloroparaffins or chlorinated paraffins that are stable organic compounds resistant to degradation and oxidation. Used as softeners and/or as flame retardants in plastics and rubbers they are harmful primarily to aquatic life.
 - Polybrominated biphenyls (PBBs) and Polybrominated diphenyl ethers (PBDEs). These biologically persistent organic compounds containing bromine are used as fire retardants in plastics, for example in housings for electrical equipment.
 - Polychlorinated biphenyls (PCBs) are biologically persistent organic compounds containing chlorine, particularly toxic to marine life. Sometimes used in rubber seals for electrical transformers and capacitors they are now being phased out and disposed off.
- Various halogenated species from solvents and paints.
- Toluene, xylene, styrene, naphthalene, ethanol, trichloroethylene and other chlorinated solvents...are harmful and contribute to greenhouse effect.
- Phosphorus derivatives, phosphates... An excess of phosphorus compounds in surface water leads to eutrophication and algal bloom.
- Nitrates from organic materials or surface runoff etc.
- Photochemical oxidants, including ozone.
- Various tiny solid or liquid particulates: soot, dust, fumes, or mist. Dust can penetrate into a person's lungs and pose health hazard. Asbestos is a well-known example.

Often, ban is more or less clear. Some regulations are unambiguous such as Eu RoHS: The European Union directive in new electrical and electronic equipment went into effect 1 July 2006 clearly pointing out some hazardous substances authorized levels:

- Lead 0.1% or 1000ppm
- Cadmium 0.01% or 100ppm
- Mercury 0.1% or 1000ppm
- Hexavalent chromium 0.1% or 1000ppm
- Polybrominated biphenyls 0.1% or 1000ppm

Those limits apply to any single (homogeneous) substance that could be separated mechanically, for example, the case of a radio or the sheath on a cable. If the one or the other contains more than 0.1% of PPB, the entire cable or radio fail the requirements of the RoHS directive. Some other examples as zinc are not so clear. In 1993 the Dutch National Institute of Public Health and Environmental Protection (RIVM) presented an 'Integrated Criteria Document' for zinc, recommending for water a 'desirable' level of 9 µ/l and a maximum allowable concentration of 25 µ/l. In 1995, zinc and zinc derivatives were included in a priority list of rubber chemicals compiled by the Swedish Environmental Protection Agency, which should be replaced or used restrictively. In 1995, zinc and zinc oxide were placed on the second European list of priority substances in the EU Risk Assessment Programme.

In June 2002 the German Standard DIN 18035-7 "Sports Grounds, Part 7" "Artificial Turf Areas" was published. According to this standard, two leaching tests are required for post-consumer tyre rubber granulates used as infill material for artificial turf and the following limits are set in leachates:

- 0.5 mg/l after leaching with deionized water (DIN 38414-4)

- 3 mg/l after leaching with water saturated with CO₂

Between 1998 and 2004, draft Assessments were produced and responses put forward by the zinc chemical and rubber industries.

Since 29 April 2004 (see Council Directive 2004/73/EC, relating to the classification, packaging and labelling of dangerous substances) zinc oxide is officially classified as "Dangerous for the Environment" with the risk phrase "Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment", and with the safety advice "This material and its container must be disposed of as hazardous waste" and "Avoid release to the environment. Refer to special safety instructions/safety data sheets". Rubber compounds containing more than 2,5 % in total of zinc chemicals or other chemicals classified as R50/63 (such as IPPD) are classified as "Toxic to aquatic organisms, may cause long-term effects in the aquatic environment".

Asbestos, composed of minerals, became increasingly popular in the late 19th century due to its resistance to heat, electricity and chemical damage, sound absorption and tensile strength. The inhalation of asbestos fibres can cause serious illnesses, including mesothelioma and asbestosis. Since the mid 1980s, many uses of asbestos are banned in many countries. Substitutes such as other mineral fibers, natural or synthetic (glass or rock wool, ceramic fibers, whiskers) or organic fibers (Kevlar pulp, polybenzoxazole) and carbon fibers are required more study. There is a broad choice of solutions excluding hazardous substances included in the RoHS but, of course, the chosen solutions must meet general regulations and trends related to plastics and additives. In brief:

- Technically: it is necessary to converge on a difficult balance of flame retardant properties and low smoke emission with constraints concerning opacity, toxicity and corrosivity of fumes
- Legally: standards, regulations, specifications are complex, evolutionary, variable according to countries and industrial sectors.
- FR additives, as the others, must satisfy environmental trends and regulations.
- FR can modify mechanical properties and aesthetics.

The first question is to decide between halogen-free and halogen-containing systems. The second question concerns the possible use of phosphorous additives. Among the main FRS without claiming to be exhaustive, we can distinguish:

- Mineral fillers and additives: Aluminum trihydroxide (ATH), magnesium hydroxide, boron derivatives are the best known but tin derivatives, ammonium salts, molybdenum derivatives, magnesium sulphate heptahydrate are more or less used.
- Phosphorous additives: Red phosphorous, phosphates ester plasticizers, ammonium polyphosphate, melamine phosphates, and melamine pyrophosphate. Some of them can be halogenated also.
- Inorganic complexes or compounds such as, for example Kemgard® products, flame retardants/smoke suppressant additives including zinc molybdate, calcium zinc molybdate, zinc oxide/phosphate, zinc molybdate-magnesium silicate, zinc molybdate/magnesium hydroxide.
- Nano fillers: nanosilicates, carbon nanotubes, nano oxides such as, for example MARTINAL® & MAGNIFIN® CHAR™ launched by Albemarle and based on nanotechnology.
- Halogenated derivatives: Brominated organic compounds are the most used often in combination with antimony trioxide to develop a synergistic effect. Unfortunately, these combinations can generate a lot of smoke and toxic fumes, which are unacceptable for many regulations and standards. Moreover, PBB and PBDE are not RoHS compliant.
- Brominated polystyrene is marketed as fire retardant additive.

The EU's RoHS bans Polybrominated biphenyls (PBB) and/or Polybrominated diphenyl ethers (PBDE) flame retardants but other brominated FR can be used. Saytex HP-3010, brominated polystyrene flame retardant is claimed complying with the RoHS Directive.

FR solutions must be carefully studied according to the whole fire specifications on the one hand and the other mechanical, electrical, optical properties on the other hand. So, for a panel of FR grades based on PVC:

- Oxygen index can increase from 38% up to 64% but in the same time, smoke parameter can be divided by 2 or magnified by 1.5.
- Heat stability and impact strength are altered or slightly improved.

For a panel of halogen-free FR grades based on EVA:

- Oxygen index can increase from 18% for the neat EVA up to 32% for FR grades with an improved fire rating of

V2 or V0 and a CO yield divided by 2 or 4.

FR polymer grades must be considered as the simplest solution. For example, VAMPTECH, Italy, has launched grades of flame retardant glass reinforced polyamide (PA) that are free from halogens, phosphorus and heavy metals. VAMPAMID 6 3028 V0 and VAMPAMID 66 3028 V0 are 30% glass filled PA 6 and PA 66, respectively. The company claims they will help manufacturers meet standards such as the Eu's Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS).

PCBs or Polychlorinated biphenyls are organic compounds with several chlorine atoms attached to biphenyl composed of two benzene rings. They were used as coolants and insulating fluids for transformers and capacitors, stabilizing additives in flexible PVC coatings of electrical wiring and electronic components...until their ban in the 1970s. PCBs are classified as persistent organic pollutants which bio accumulate in animals.

Commercial grades were marketed as Aroclor, Askarel, Clophen, Kanechlor, Phenoclor, Pyralene, Santotherm... PCBs can be replaced in transformers by another fluids, subject to all other requirements, such as, for example:

- Mineral Oils
- Silicones
- Blends of esters of pentaerythritol and fatty acids

Due to the very different chemical structure of those fluids, the polymer parts in the transformer can be dramatically altered.

Lead- and cadmium-based pigments have been used extensively due to their relatively low cost coupled with their good fastness properties and reasonable processability. However, to respond to social and environmental concerns and regulations many manufacturers eliminate the lead and cadmium pigments.

The Eu Substance Directive 67/548/EEC classifies aromatic distillates as 'carcinogenic' and allocates the risk phrase R45 (may cause cancer) and the label T (skull and cross-bones). The environmental problem is significant seeing that for a nation as Sweden, the total tire wear was estimated at 10 000 t in 1994, that is to say, potentially, some tonnes of polycyclic aromatic hydrocarbons.

Plasticizer suppliers study the use of safer oils:

- Free of carcinogenic products.
- Available in large quantities.
- Competitive.
- Efficient in rubber processing and finished rubber goods.

It appears that the replacement is possible with slight formulation adjustments.

There is not a single answer because of the versatility of elastomers and crosslinking.

The activity of zinc oxide can be boosted with:

- Other metal oxides. For example STRUKTOL® ZIMAG 29/43 consists of 29% zinc oxide, 43% magnesium oxide and 28% wetting and dispersing agent. It is used as activator for crosslinking of polychloroprene. The suggested dosage depending on the required cross-linking density is 4 - 8 phr, that is to say 0.6 to 1.2% of zinc in a 50% reinforced compound.
- Anti-reversion agents such as AKTIVATOR 73 (zinc soaps) and PERKALINK 900 (biscitraconimide) allow formulating truck tyre compounds with zinc content below 1%.
- Combination of cetyltrimethylammonium malleate and an anti-reversion agent allows formulating compounds with zinc content below 0.6%.

In sulphur vulcanization of SBR. CaO and MgO are conceivable alternatives to ZnO albeit a lower cure rate and some differences concerning the state of cure. Nitrosamines can be produced and emitted at the workplace by reaction of some accelerators during the vulcanization of rubbers. They can also be present in finished goods. Certain nitrosamines are banned at the workplace and into rubber goods for some applications.

Low to nil nitrosamine emitting accelerators have been developed for the vulcanization of various rubbers, for example:

- Tetrabenzylthiuram disulfide (Westco TBzTD, Benzyl Tuex® ...) a fast curing primary or secondary accelerator in natural rubber (NR), SBR, nitrile rubber (NBR) emits low to nil nitrosamine; is not carcinogenic and leads to acceptable scorch times.
- Zinc dibenzylthiocarbamate (Westco ZBEC, Arazate® ZnDBzC...) is convenient as non-discolouring and non-staining primary or secondary accelerator for natural rubber (NR), butyl rubber (IIR), SBR, EPDM, natural and synthetic lattices. It emits low to nil nitrosamine and leads to acceptable scorch times.

Lead is used in EPDM for wire and cable coatings to neutralize the eventual chlorine ions coming from residues of catalysts. Under the pressure of environmental regulations, California 's Proposition 65 for example, alternatives are studied (D. KANG and All, ACS, Oct. 2003, paper 115) replacing lead stabilizer with hydrotalcite or a system hydrotalcite and coagent. Table 1 displays swelling in boiling water, and electrical and mechanical properties after ageing showing that lead stabilizer can be replaced by a combination of hydrotalcite and coagent.

Lead stabilizers can be replaced, if there are no other restrictions, with calcium/zinc soaps or barium/zinc soaps that are not banned by the RoHS directive. If we query the SpecialChem database, 20 stabilizer producers (see table 2) market more than 100 grades of such stabilizers. About 60% are calcium/zinc soaps and 40% are barium/zinc soaps. Some producers market also combinations of barium/cadmium or barium/cadmium/zinc derivatives but cadmium is banned by the RoHS directive.

It must be noticed that there are numerous threats relating to zinc leaching particularly in water wastes. Some aquatic species have been shown to be sensitive to very low levels of zinc, and concerns about the release of zinc to aquatic eco-systems have developed over the past years. The following examples of directives, regulations, drafts etc. are not exhaustive and other requirements are to be searched by the reader for his own problem.

Small amounts of volatile materials are added to polyurethanes as blowing agents to produce foams with better performance characteristics, notably thermal insulation. Until the early 1990s, many halogenated blowing agents, such as trichlorofluoromethane (CFC-11) were used but because of their impact on ozone depletion, the Montreal Protocol led to a greatly reduced use. Other haloalkanes, such as the hydrochlorofluorocarbon 1,1-dichloro-1-fluoroethane (HCFC-141b), were temporarily used as substitutes until their phase out under the IPPC (Integrated Pollution Prevention and Control) directive on greenhouse gases and by the Volatile Organic Compounds (VOC) directive of the EU in 1997. By the late 1990s, they were partially replaced by other blowing agents such as carbon dioxide, pentane, 1,1,1,2-tetrafluoroethane (HFC-134a) and 1,1,1,3,3-pentafluoropropane (HFC-245fa).

Molecules can be banned for carcinogenic, mutagenic, reproductively-toxic effects; pollution of air, water, land; greenhouse effect, ozone depletion. Ban can be total or partial depending on the countries and polymer applications with two basic consequences for plastics and rubbers: the need to use substitutes in polymer formulation if the ban concerns an additive or the need to change the processing method if the banned product is used in the process.

(Source: SpecialChem)