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HAZARDOUS PROPERTIES OF MINERAL AND ORGANO-MINERAL PLASTIC ADDITIVES AND MANAGEMENT OF HAZARDOUS PLASTICS

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ABSTRACT

Many plastic additives are mineral or organo-mineral substances having functions as pigments, heat stabilizers, flame retardants, process adjuvants and the like. Are additivated plastics hazardous when they become waste? Data from the Plastic Additives Initiative, a joint industry and EU effort, was used, along with substance hazard statements from the ECHA website and hazard properties from the waste classification. 20 elements of 91 substances, namely Al, B, Ba, Bi, Cd, Co, Cr, Cu, F, I, Li, Mn, Ni, Pb, Pr, Sb, Sn, Ti, V and Zn were selected, and their additives used in 11 polymers, considered. Of the 91 substances selected, 57 are non-hazardous or are hazardous but used at too low concentration to render the plastic hazardous when it becomes waste. 34 substances (= 37% of 91) are hazardous and make plastics hazardous as waste. These are mainly heat stabilizers (for PVC), or pigments and flame retardants (for all polymers). The sorting of these plastics by the mineral concentration of their additives with online XRF is theoretically achievable. With data from previous papers, 63 additives (= 27% of 233) make plastic hazardous. The brominated flame retardants are the less documented. Only essential use should be allowed for pigments. Waste management today should focus on turning waste into non-waste, not waste leakage. With occupational safety and health regulations during processing, and with product regulations during its second life, the material should be managed as another hazardous or non-hazardous (virgin) raw material, and given end-of-waste status when it enters the loop.

1. INTRODUCTION

Additives are substances that improve the properties of plastics. Their use is generalised. They can be hazardous. More and more complete lists of substances used in plastic formulations are published and three of them are shortly presented in this introduction. It is underlined in these documents that numerous substances are hazardous, having as pure substance one or more hazard statement codes in the substance classification. The domain is so vast that the reader is invited to consult the available reviews and literature as in the journal Plastic Waste and Recycling.

European authorities are promoting progress towards a “toxics-free environment” (EC, 2020). Professionals fear that this "zero risk" approach is in fact a “hazard only” approach and entails significant difficulties for the circular economy, going as far as the impossibility of sorting waste fractions with very low concentration, losses of material in their loop and the costs of recycling which must devalue these fractions or incinerate or landfill these now non-recyclable fractions (EURIC, 2019). Waste could be treated by risk as products, according to REACH. It is therefore very important to develop applications in which materials containing a certain content of critical compounds can be used safely (Friege et al., 2021).

To progress towards a toxic-free environment or a risk-controlled circular economy, the substances must be prioritised. An early example is the report of Hanssen et al. (2013) of COWI consulting company, intended to be a brief handbook on plastic types and hazardous substances in plastics, their function, uses, concentration, release patterns, and alternatives, and focusing on 43 substances and families of substances. A review of POP substances, their occurrences in plastics and their potential management, including perfluorinated POPs, is presented in EC (2021).

One option is to restrict the use of hazardous additives according to the concept of “essential uses.” This concept has been applied in the context of the Montreal Protocol under which a use of a controlled substance should qualify as “essential” only if: (1) it is necessary for health and safety or

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critical for the functioning of society (which encompasses cultural and intellectual aspects); and (2) there are no available technically and economically feasible alternatives or substitutes acceptable from the standpoint of environment and health (Weber et al., 2022). The concept of "essential uses" could also be applied to the management of other chemicals or groups of chemicals of concern, including hazardous or otherwise problematic additives that are not yet completely phased out. Only for those essential uses, where currently no substitute is available, should these additives be allowed in controlled material cycles. For uses that do not qualify as essential, hazardous additives should be substituted with safer alternatives (Weber et al., 2022).

Another option is to list all the substances that are hazardous. The three below-mentioned contributions are very large reviews of the substances that are used, and recommendations for their management to reduce (eco)toxic substances in the material flows.

(i) Aurisano et al. (2021) provide a list of more than 6 000 chemicals reported to be found in plastics and an overview of the challenges and gaps in assessing their impacts on the environment and human health along the life cycle of plastic products. They further identified 1 518 plastic-related chemicals of concern, which should be prioritized for substitution by safer alternatives. At last, the authors propose five policy recommendations for plastics:

- a transparent supply chain management
- a global and overarching regulatory framework for plastics and related chemicals, in support of a circular economy for plastics
- funds to invest in mechanisms to coordinate and support the transition of industries
- funds in research for efficient manufacturing of virgin and recycled plastics
- educate and support citizens, companies, and investor.

(ii) Wiesinger et al. (2021) investigate plastic monomers, additives, and processing aids on the global market based on a review of 63 industrial, scientific, and regulatory data sources. They identify +10 000 relevant substances and categorize them based on substance types, use patterns, and hazard classifications wherever possible. Over 2 400 substances are identified as substances of potential concern as they meet one or more of the persistence, bioaccumulation, and toxicity criteria in the European Union. Many of these substances are hardly studied (266 substances), are not adequately regulated in many parts of the world (1 327 substances) or are approved for use in food-contact plastics in some jurisdictions (901 substances). The possible ways forward are:

- establishing a centralized knowledge base
- ensuring transition to a safe and sustainable circular plastic economy (mainly information on and avoidance of hazardous substances)
- expanding and harmonizing regulatory efforts.

(iii) Weber et al. (2022) wrote an informative document for the UNEP Plastic Pollution conference (UNEP, 2022). It is a comprehensive review of all the aspects of plastics and chemicals in plastics, including capacity strengthening in particular in developing countries. With the two previous studies, they identified over 13 000 chemicals associated with plastics and plastic manufacturing across a wide range of applications, amongst which over 2 400 plastic monomers, additives and processing aids of potential concern based on their hazardous properties, with potentially significant adverse impacts. They claim access to information regarding the presence and quantity of chemicals in plastics, emissions and releases of chemicals from plastic products, as well as product use patterns. The authors rise the question of better capture of realistic exposure conditions in [hazard, exposure and risk] assessments, including exposure to chemical mixtures via multiple pathways, which would further enable science-based policy decisions that sufficiently safeguard human and environmental health.

This paper proposes, rather than lists of dangerous additives (hazard approach only), a risk approach: detecting the additives which make the plastic dangerous at their functional concentration and managing these plastics in controlled industrial loops (risk approach) so that the probability of exposure to hazards is very low, together with the phasing out substances of concern at the design stage.

Where to start identifying hazardous additivated plastics? In our opinion, reference methods like the CLP and the EU Waste classification should be used. That latter classification is derived from EU substances and mixture classification so-called CLP (Classification, Labelling and Packaging of chemicals and mixtures, EC, 2008) which is the aligned European version of the Globally Harmonised System (GHS) of the UN. The GHS is a single worldwide system for classifying and communicating the hazardous properties of industrial and consumer chemicals. The hazardous quality or not of the additivated plastic(s) depends on the properties of the additives and their concentration in the material. That later information is scarcer. Therefore, the plastics can be managed with such lists only as a first approach. It is proposed here to first assess the additives that renders plastic hazardous (according to the EU waste classification) when used at their functional concentration.

In this study, from an official list of 418 additives used in the European Union, mineral and organo-mineral additives with typically toxic or ecotoxic elements were selected, their hazard statement retrieved from the European Chemicals Agency site, and for the hazardous ones, their typical concentration in plastics (11 polymers) compared with the concentration limits making waste hazardous in the EU waste classification system.

This paper closes a series of four papers devoted to the hazardous additives in plastics: (i) brominated flame retardants (Hennebert 2021a), (ii) phosphorous, chlorinated, nitrogen and mineral flame retardants (idem 2021b), (iii) plasticisers (idem 2022a), and (iv) other mineral and organo-mineral additives (this paper). A synthesis of the hazard of the most important groups of additives is presented, and their management discussed, with a structured approach of the many possibilities of management. The objective of the waste regulation is discussed, as well as the opinion that, as soon as they enter in the loop of modern collection and industrial recycling, the additivated plastics, hazardous or not, should be managed as every raw material. The limitation of the quantities that can be present at a civic amenity site at the same time (1 tonne in France, not enough for profitable transport), the specific transport documentation, the special procedure for cross-border transport (not all countries not have all the technologies for the treatment of waste), the specific status of the recycling facilities, the undefined status after sorting and treatment are brakes and costs that limit the recycling of these materials.

1.1 Abbreviations

ABS	Acrylonitrile butadiene styrene
AO	Antioxidants
AS	Antistatic
CAS no	Chemical Abstract Service number
CLP	Classification, Labelling and Packaging of chemical substances and mixtures
EC no	European Community number
ECHA	European Chemicals Agency
ELV	End-of-life vehicles
F	Filler
FC	Functional concentration (of an additive in a polymer)
FR	Flame retardants
H	Hazardous
Hxxx	Hazard statement code of a substance
HP	Hazard property of waste
HS	Heat stabilisers
HSC	Hazard statement code
L	Lubricant
NH	Non-hazardous
NIR	Near infra-red spectroscopy
NU	Nucleating agents
OBL	Obligations in EU regulations
OF	Other functions
OS	Other stabilisers
PA	Pigments agents
PAM	Polyamide (Nylon®)
PAI	Plastic Additive Initiative (joint action of the EU and industry)
PC	Polycarbonate
PET	Polyethylene terephthalate
PL	Plasticisers
PMMA	Polymethylmetacrylate
Polyolefin-I	Polyethylenes
Polyolefin-II	Polypropylenes
PS - (E)PS	(Expanded) polystyrene
PUR	Polyurethane
PVC (rigid)	Polyvinylchloride
PVC (soft)	Polyvinylchloride (softened)
REACH	Registration, Evaluation and Authorisation of Chemicals
WEEE	Waste of electrical and electronic equipment
XRF	X-ray fluorescence spectroscopy

2. MATERIAL AND METHODS

2.1 Data

The Plastic Additives Initiative (PAI), a collaboration between the European Chemicals Agency - ECHA and the plastics industries delivered in 2019 a list of 418 additives currently used in products in the EU, along with their function(s), the polymer(s) they improve, and their functional concentration(s) (ECHA, 2021a). The excel file is no longer available, but the list of additives by function is available (with polymer and functional concentration) and a file can be easily reconstructed from the different screens of ECHA (2021). 20 elements were selected. For the 91 additives containing these 20 elements, the hazardous properties of human toxicity and ecotoxicity were collected from the ECHA open-access registration site of chemicals in the EU (ECHA 2021b). When their functional concentration is mentioned, it is compared with the concentration that makes a waste hazardous for the 15 hazard properties of waste (EU 2014, 2017).

2.2 Selection of the elements

Elements of the additives were computed from the chemical formula. This paper considers 20 elements, namely Al, B, Ba, Bi, Cd, Co, Cr, Cu, F, I, Li, Mn, Ni, Pb, Pr, Sb, Sn, Ti, V and Zn. The excluded elements are listed below. Chromium is always Cr (III) excepted in two pigment agents with Pb where it is Cr (VI) (Table 2). For sake of simplicity, these two substances have not been counted for Cr but only for Pb.

The following elements are not included in this study:

- 3 elements of the molecular organic skeleton: C, O, H;
- 5 elements of flame retardants (that are presented in in Hennebert 2021a, b): Br, Cl, N, P and Sb of Sb_2O_3 (a flame retardant synergist);
- 7 major (dominant in earth's crust) elements, being typically not the source of hazard if part of a hazardous substance: Ca, Fe, K, Mg, Na, S, Si.

Aluminium is as well a major element, but the aluminium hydroxide has hazard statement codes, and Al is used in organo-metallic compounds. Aluminium is noted in two cases "aluminum" in the ECHA data base (CAS 101357-30-6 Silicic acid, aluminum sodium salt, sulfurized and EC 939-582-4 Fatty acids, C16-18 (even numbered), aluminum salts). These names have not been changed here.

2.3 Properties of additives and classification of additivated plastic when it becomes waste

The hazard statement codes of additive substances were retrieved from the self-reported ECHA dossier (ECHA 2022). For some substances, the ECHA mentions its own "harmonised" classification, or indicates that a re-assessment is in progress. The hazard classification of the additivated plastics as waste is done according to the EU regulations (EU, 2014; EU, 2017) with maximum concentration for some properties and (weighted) summation of concentration for other properties (HP 4, HP 6, HP 8, HP 14). A synthesis of waste classification is presented in Hennebert (2019a). It has been supposed that only one additive is used in a plastic compound. The eventual other additives are not known and hence their properties and concentration have not been considered.

The functional concentrations are not always mentioned in the PAI file. When the concentration of one additive was mentioned as "n.a." (not available), the minimal and mean concentrations of the additives with the same function in the PAI file were used for that additive (Table in Hennebert, 2021b) . The function of the additive containing cobalt is not mentioned, has not been found in the literature and is assessed to "other functions".

Some special cases are the following:

- Differences in calculations of HP 14 with H400 for products and for waste: see (Hennebert 2021b). Only zinc distearate (CAS 557-05-1, Table SI 3) has the hazard statement code H400 but not H410 and has been classified by the product approach. A M-factor of 1 has been used since no data of acute ecotoxicity are available in the REACH dossier of that substance.
- TiO_2: it is assumed here that TiO_2 in plastics is not in free fine powder 10% < 10 µm and hence not H351 Carcinogenic level 2 but embedded in the plastic matrix.
- Cr_2O_3: 15% of notifiers have declared H360, Reprotoxic level 1. A waste is HP 10 if the concentration of H360 substance is > 0.3%. No substances of chromium (III) are classified in the harmonized classification and that approach is used here.

3. RESULTS AND DISCUSSION

The occurrences of the elements and their functions is presented by decreasing order in Table SI 1. If one substance contains two or more elements of the 20 elements considered here, it is counted in this table two times or more. Al, Zn, Cr (III) and Cu accounts together for half of the occurrences (56/112), and the pigments agents are the highly dominant function (73/112).

The stabilisers are the second group (heat stabilisation with 14 additives and other stabilisers with 4 additives) and are useful for the long-lasting of the products. The flame retardants (third group with 8 additives) are important for protection of humans, equipment, and infrastructures.

From this point of the paper, the additives are counted as individual substance. A multi-element additive is counted as one substance.

3.1 The 57 non-hazardous additives or non-hazardous plastics at the functional concentrations of hazardous additives

There are 57 non-hazardous additives or non-hazardous plastics at the functional concentrations of hazardous additives. These 57 substances are presented by substance in Table SI 2 and by elements and functions in Table 1. They are pigments agents (46), heat stabilisers (4), other stabilisers (2), lubricant (2), flame retardants (1), filler (1) and nucleating agents (1).

3.2 The 34 hazardous plastics at the functional concentrations of the hazardous additives

There are 34 hazardous additives that render plastics hazardous at their maximal functional concentrations, and 28 substances that render plastics hazardous at their minimal functional concentration. These 34 substances are presented by substance in Table SI 3 and by elements and functions in Table 2. There are 8 additives with Pb (including one with Cr (VI) and one with Cr (VI) and Mo), 5 with Sn, 5 with Zn (one with B), 3 with Cd (with other elements), 3 with Al, 2 with B, 2 with Sb (one with Mn and Ti), 2 with Cu (one with I) and 1 with Co, V, Li and Mn, respectively.

They are heat stabilisers (10), pigments agents (9), flame retardants (6), other functions (3), antistatic (2), antioxidants (1), other stabilisers (1), plasticisers (1) and lubricant (1).

Pigments agents is still the second group while it is the first group for non-hazardous additives or additives that don't render plastic hazardous. These 9 pigments agents contain 12 elements (Cd, Cr (VI), Cu, Mn, Mo, Pb, Sb, Se, Ti, V, Zn and Zr). With the principle of essential (and sober) use, maybe could the use of the hazardous pigments be reduced.

For these 20 elements of 91 substances, 26 substances (= 29% of 91) or 34 substances (= 37% of 91) make the plastic hazardous (Table SI 4).

3.2.1 What polymers and what function(s)?

Of the 34 additives that renders the plastics hazardous at maximal functional concentrations, the polymers in which these additives are used are available for 24 additives. Eleven different polymers are listed in the file (Table 3).

The most additivated polymers are PVC (soft and rigid), followed by polyolefin- and -II (PE and PP) and then PAM. Soft and rigid PVCs are additivated with many substances that makes them hazardous in the waste classification (20 and 18, respectively – Hennebert 2022a).

Four groups of additives can be distinguished:

- a group of 6 pigments agents and 1 flame retardant, antistatic, UV/light stabilizer (1) suitable for all the 11 polymers;
- a group of 10 heat stabilisers specific for PVC soft and rigid, including one for Polyolefin-I;
- a group of 5 substances lubricant, flame retardants, antistatic, other stabiliser and pigments agents of diverse polymers;
- 2 additives specific to PAM and PET, respectively.

3.2.2 Ranking hazard properties of hazardous mineral and organo-mineral additivated plastics

The prevalence of hazard properties at the functional concentration of these mineral and organo-mineral additives is presented in Table SI 4.

The most frequent hazard property is HP 14 'Ecotoxic': 41% (= 24/58) of the hazardous plastics are hazardous at least by HP 14. This agrees with the general finding that 50% of the hazardous waste are classified at least HP 14 when the M-factors are used, as in the product classification (Hennebert 2013, 2014). The second most frequent hazard property is HP 10 'Toxic for reproduction' (31% of the hazardous plastics = 18/58), with a maximal concentration of 0.3% for H360 substances, and 3% for H361 substances. The other properties are less frequent: HP 5

TABLE 1: The elements of the 57 additives that are not hazardous or that are used at concentrations lower than the concentration making the plastics hazardous (by decreasing occurrences of elements and function).

Number of substances								
Element(s)	**Pigments agents**	**Heat stabilisers**	**Lubricant**	**Other stabilisers**	**Nucleating agents**	**Flame retardants**	**Filler**	**Total**
Cu	9							9
Al	4		1	1		1	1	8
Zn	2	3			1			6
Cr (III)	4							4
Ba	3							3
Mn	3							3
Al P	2							2
F	2							2
Sn	1	1						2
Ti	2							2
Bi V	1							1
Co	1							1
Co Al	1							1
Co Zn Al	1							1
Cr (III) Co	1							1
Cr (III) Cu	1							1
Cr (III) Ni	1							1
Cr (III) Sb Ti	1							1
Cr (III) W Ti	1							1
I				1				1
Ni	1							1
Sb Ni Ti	1							1
Zn Al			1					1
Zn Cr (III)	1							1
Zn Cr (III) Al	1							1
Zr Pr	1							1
Total	**46**	**4**	**2**	**2**	**1**	**1**	**1**	**57**
Total%	81%	7%	4%	4%	2%	2%	2%	100%

'STOT', HP 4 'Irritant' for skin or eye (not relevant if embedded in a polymeric matrix), as well as HP 8 'Corrosive'. Three plastics are HP 7 'Carcinogenic' (maximal concentration 0.1% H350, 1% H351: diantimony trioxide (flame retardant), lead sulfochromate yellow and lead chromate molybdate sulfate red (pigments)), and one plastic is HP 11 'Mutagenic' (maximal concentration 0.1% H340, 1% H341; dibutyltin dilaurate (heat stabiliser)). All these substances are documented in Table SI 3.

3.3 Synthesis of assessment of additives that makes plastics hazardous

The results of this paper can be grouped with the assessment of brominated flame retardants (Hennebert, 2021a), other flame retardants (Hennebert, 2021b), and plasticisers (Hennebert, 2022a). The results of the assessment of these 233 additives are presented in Table 4. Brominated flame retardants are clearly less publicly documented than the other families, despite having the highest absolute and relative number of substances with on-going (re)assessment by ECHA. In total, 63 additives (= 27% of 233) make plastic hazardous at their maximum functional concentration, with the EU waste classification. Mineral and organo-mineral additives are the most numerous group that makes the plastic hazardous. The efforts towards a toxic-free environment (EC 2020) could focus first for plastic additives on these 63 substances, classified by using their functional concentrations mentioned by the producers or the importers and according to the reference methods of the EU, and hence not questionable. The progress will be probably easier than from large lists of 6 000, 10 000 or 13 000 substances (see Introduction) with unfortunately few data on actual use.

3.4 Sorting of the plastics with mineral and organo-mineral additives

Are the elements of these additives detectable by X-ray fluorescence? The lowest functional concentration of the

TABLE 2: The elements of the hazardous 34 additives that are used at concentrations higher than the concentration making the plastics hazardous.

Number of substances										
Element(s)	**Heat stabilisers**	**Pigments agents**	**Flame retardants**	**Other functions**	**Antistatic**	**Plasticisers**	**Lubricant**	**Antioxidants**	**Other stabilisers**	**Total**
Pb	5			1						6
Sn	5									5
Zn					1	1	1	1		4
Al			3							3
B			1		1					2
Cd Se		1								1
Cd Zn		1								1
Cd Zr		1								1
Co				1						1
Cu		1								1
Cu I									1	1
Li				1						1
Mn		1								1
Pb Cr (VI)		1								1
Pb Cr (VI) Mo		1								1
Sb			1							1
Sb Mn Ti		1								1
V		1								1
Zn B			1							1
Total	**10**	**9**	**6**	**3**	**2**	**1**	**1**	**1**	**1**	**34**
Total%	29%	26%	18%	9%	6%	3%	3%	3%	3%	100%

mineral additives is 0.1% corresponding to concentration of 0.01-0.08% of the element(s) of the additives. These concentrations are detectable with hand-held field or laboratory apparatus (about 10 mg/kg = 0.001% with some seconds of measurement). For on-line sorting instrument like Redwave (Redwave, 2022), the time of measurement is much shorter, and the limit of detection is much higher, being about 1.5% in practice. The efficiency of the sorting depends then on the distribution of the concentratiln in the plastic shreds: if it is bimodal with a non-additivated group with zero or close to zero concentration and an additivated group with a functional concentration > 1.5%, the sorting is efficient. An example for Br in cathode ray tubes shreds is given in Hennebert and Beggio (2021c).

Not considering the too light elements B and Li whom the additives are not detectable when B and Li are not associated with another heavier element, of the remaining 32 hazardous additives making plastic hazardous at maximal functional concentration (Table SI 5) , 17 have a minimal FC higher than 1.5% and 27 have a maximal FC higher than 1.5%. The corresponding elements of the 32 additives detectable by XRF are Al, Co, Cr, Cu, I, Mn, Pb, V and Zn. The sorting of these plastics by the mineral concentration of their additives is therefore theoretically achievable but the practicality (interference of dust, geometry of the shreds, presence of a coating layer) and the economic return of such operation should be checked. It is not practiced today to our knowledge.

3.5 Management of the POP, hazardous and non-hazardous plastics

A partial summary of the limitation of unintentional concentration of substances in products for POP substances and the four hazardous elements in WEEE is presented in (Hennebert, 2021). There are nevertheless exemptions in the POP regulation (EU, 2019). The limitations for four phthalate plasticisers (EU, 2018a) are summarised in (Hennebert, 2022a). A first step is phasing out substances of concern at design stage (EURIC 2019).

For hazard waste classification, the general method is synthetised in Hennebert (2019). Some POPs make the mixture that contain them hazardous (same reference). The hazardous waste classification has been applied to substitutive brominated flame retardants (BFR) in (Hennebert 2021a - Table 4), to Cl, P, N and some mineral flame retardants in (Hennebert 2021b – Table 3 to 6), to plasticisers in (Hennebert 2022a - Table 3) and to mineral additives in this paper (Table 3 and Table SI 3). In total 63 additives proposed in the EU are used in concentration that make the mixture hazardous (Table 4 of this paper). Waste of EEE and end-of-life vehicles (ELV) are hazardous; the parts containing POPs or that are hazardous must be separated during dismantling (EU 2018b).

The management of plastic as waste depends primarily on their concentration in regulated substances. If they con-

TABLE 3: The polymers and functions of 24 substances with documented functional concentration that make plastic hazardous, (no data of polymers for the other 12 substances) (FC = functional concentration; polymers: see abbreviation list; the colours illustrate the main features of the groups).

Substance	Elt	Function	FC (%)	PVC (soft)	PVC (rigid)	Polyolefin-I	Polyolefin-II	PAM	PET	ABS	PUR	PC	IPS	PMMA	Total 11 polymers
Group 1: Pigments (6) and Flame retardant, Antistatic, UV/light stabilizer (1) for 11 polymers															
Cadmium zinc sulfide yellow	Cd	Pigments agents	5	x	x	x	x	x	x	x	x	x	x	x	11
Silicic acid, zirconium salt, cadmium pigment-encap-sulated	Cd	Pigments agents	5	x	x	x	x	x	x	x	x	x	x	x	11
Cadmium sulfoselenide red	Cd	Pigments agents	5	x	x	x	x	x	x	x	x	x	x	x	11
Lead chromate molybdate sulfate red	Cr	Pigments agents	5	x	x	x	x	x	x	x	x	x	x	x	11
Lead sulfochromate yellow	Pb	Pigments agents	1	x	x	x	x	x	x	x	x	x	x	x	11
Manganese antimony titani-um buff rutile	Sb	Pigments agents	5	x	x	x	x	x	x	x	x	x	x	x	11
Zinc oxide	Zn	Flame retardant; Antistatic; UV/ light stabiliser;	5	x	x	x	x	x	x	x	x	x	x	x	11
Group 2: Heat stabilisers of PVC (9) and PE (1 of the 9)															
Pentalead tetraoxide sulphate	Pb	Heat stabilisers	2	x	x										2
Tetralead trioxide sulphate	Pb	Heat stabilisers	2	x	x										2
Dioxobtearateato)trilead	Pb	Heat stabilisers	2	x	x										2
Sulfurous acid, lead salt, dibasic	Pb	Heat stabilisers	2	x	x										2
Fatty acids, C16-18, lead salts	Pb	Heat stabilisers	2	x	x										2
Methyl (Z,Z)-8,8-dibutyl-3,6,10-trioxo-2,7,9-trioxa-8-stannatrideca-4,11-dien-13-oate	Sn	Heat stabilisers	2	x	x										2
2-ethylhexyl 10-ethyl-4,4-di-octyl-7-oxo-8-oxa-3,5-dith-ia-4-stannatetradecanoate	Sn	Heat stabilisers	2	x	x										2
2-ethylhexyl 10-eth-yl-4-[[2-[(2-ethylhexyl) oxy]-2-oxoethyl]thio]-4-octyl-7-oxo-8-oxa-3,5-dithia-4-stan-natetradecanoate	Sn	Heat stabilisers	2	x	x										2
Ethyl 9,9-dioctyl-4,7,11-tri-oxo-3,8,10-trioxa-9-stannatet-radeca-5,12-dien-14-oate	Sn	Heat stabilisers	2	x	x										2
Dibutyltin dilaurate	Sn	Heat stabilisers	3	x	x	x									3
Group 3: Flame retardants, pigments agents, Lubricant, Antistatic, Other stabilizer, of diverse polymers (5)															
Diantimony trioxide	Sb	Flame retardants	8	x		x	x	x		x					5
Hexaboron dizinc undeca-oxide	B	Flame retardants	0–3 - 0.4			x	x	x							3
Aluminium hydroxide	Al	Flame retar-dants; Pigments agent	0.–5 - 50.0			x		x			x				3
Disodium tetraborate, anhydrous	B	Flame retardant; Antistatic; Other stabilisers	5	x		x	x								3
Zinc distearate	Zn	Lubricant	0–5 - 1.0	x	x			x	x						4
Group 4: Additives specific to PA (Other stabilisers) 51° and PET (function not available) (1)															
Copper iodide	Cu	Other stabilisers	0.5					x							1
Cobalt bis(2-ethylhexanoate)	Co	(not available)	n.a.						x						1
Total 24 substances				**20**	**18**	**12**	**10**	**12**	**9**	**8**	**8**	**7**	**7**	**7**	**118**

TABLE 4: Synthesis of assessment of flame retardants, plasticisers and organo-mineral additives that makes the additivated plastics hazardous.

Functions and additives (source of data)	Number of additives	Number of documented functional concentrations FC	Number of plastics hazardous at maximum FC (% of the number of additives)	Additives with on-going assessment by ECHA	Reference
Flame retardan−s - Brominated (main Producers catalogs + PAI*)	41	4	4 (= 10%)***	12	Hennebert 2021a,b
Flame retardan−s - Cl, P, N, Sb, B (P, Zn), Al (Na), Mg, Ca (PINFA** + PAI)	32	16	8 (= 25%)	5	Hennebert 2021b
Plasticisers (PAI)	69	47	17 (= 25%)	8	Hennebert 2022a
Mineral and Organo-mineral additives (PAI)	91	74	34 (= 37%)	2	This paper
Total	233	141	63 (= 27% of 233)	27	This paper

** PAI = Plastic Additives Initiative*
*** PINFA = Phosphorus, Inorganic and Nitrogen Flame Retardants Association*
**** underestimated: 10 additives or blends without CAS number, 2 without dossier in ECHA, 10 without Hazard Statement Code in the dossier, 6 under reassessment by ECHA*

tain POP substances above Annex IV of POP regulation, the POP substances (and in practice the additivated plastics) must be "destroyed or irreversibly transformed". The PVC and PUR containing one of the four regulated phthalates with a concentration > 1000 mg/kg cannot be recycled. Hazardous plastics can be recycled.

The first step is the separate collection or the separation of plastics from other materials (eventually after shredding) of as much plastic as possible. Landfilling of plastics will be forbidden in 2025 in the EU, as any recyclable material (EC, 2014), according to the hierarchy of waste management (EU, 2008-2018). The management options for plastics with additives used in concentration making the plastic hazardous or not could be:

1. Re-use as article
2. Sorting if the wastes are mixed and recovery of the polymer or the additives of the sorted fraction
   (a) By colour: UV/visible detectors
   (b) By (additivated) polymer: X-ray transmission density, float/sink baths density, near infra-red (NIR) detectors (not effective with black plastics)
   (c) By polymer: float/sink baths density, near infra-red (NIR) detectors (not effective with black plastics)
   (d) By element of the additive(s): manual X-ray fluorescence (XRF), online XRF, and at laboratory stage by NIR (for instance Bonifazi et al., 2020)
3. Mechanical recycling: use in new product as additivated thermoplastic polymer if available in homogeneous prepared batches (from production falls, from selective demolition like window frames in PVC with lead stabiliser, pipes..., or from sorting systems) or sorted batch. This option is relevant for thermoplastics but not for thermosets (polyurethane, polyester, epoxy, silicone, rubber)
4. Chemical recycling: Purification of some polymer by selective dissolution and precipitation, or solvolysis (for instance CreaSolv® process of Fraunhofer Institute applied to brominated polystyrene and in pilot scale to plasticised PVC). Purification of the separated additive should be considered, as the hydrogenation of restricted phthalates of PVC
5. Chemical feedstock or fuel recovery from mixed plastics or sorted fractions: Pyrolysis or gasification and recovery of the liquid phase or the gas phase. Typically, the metallic elements remain in the char while the unwanted halogens are present in the liquid phase and in the gas phase
6. Element(s) recovery: Incineration with energy recovery and recovery of elements in ashes and fumes or fly ashes and air pollution control residues. For instance, Sb in Umicore copper smelter facility fed with WEEE plastics (Umicore 2022), and Br in ICL facility combined with the PolystyreneLoop facility (Polystyreneloop 2022)
7. Energy recovery: Incineration, typically prepared as solid recovered fuel for furnaces, or mixed in household waste or commercial waste in municipal solid waste incinerators
8. Landfilling of mixed plastics or sorted fractions
   (a) Plastics are not in the list of accepted waste and total organic carbon TOC must be lower than 3% in landfill for inert waste (EC, 2003) and organic material is restricted in landfill for hazardous waste (loss on ignition < 10% and total organic carbon < 6%, excluding in practice plastics)
   (b) Non-valorisable fractions in technical and economic conditions of the moment (like fluff of foam and textiles from shredding of automotives, and thermosets that do not be remelt and cannot be remoulded) are accepted in landfill for non-hazardous waste.

An additional case is the recovery of the elements of the electronic parts of the printed circuit boards (not the additive of the plastics), requiring the separation of the volatile phase of the plastics and the glass fiber part of the epoxy plates by pyrolysis, before being processed by a non-ferrous metal foundry. A discussion of waste, landfilling, sorting, mechanical recycling and chemical recycling of plastics is presented in (Hennebert, 2022a).

Risk method for reusing and storing of non-hazardous plastics in a linear or circular economy

The management of non-hazardous waste (frequently containing contaminants below the concentration limits which render the waste hazardous) is in practice carried out according to a risk approach and the resulting specific concentration limits must be observed for the disposal pathway or expected valorisation (Hennebert, 2022b). Concentration limits can apply to total concentration, be related to bioavailability (not defined for waste), or to leachable concentration. This approach is not specific to plastics. Research on the hazard and risk of plastic objects or (micro)particles (without or with additives) in the natural environment is active. Methods and concentration limits for polymer debris entering the terrestrial environment (mainly tire wear in traffic dust and synthetic textile fiber emitted during washing and present in sewage sludge used for land fertilisation) should be developed, based on scientific evidence and a risk approach. In the latter case, the conflict of objectives (protect the soil/recycle nutrients) must be arbitrated by the data, and technological solutions such as a filter at the exit of washing machines (compulsory in France in 2025 for new machines, RF 2020) must be promoted to resolve the conflict.

Risk method for management of hazardous plastics in a circular economy

The waste status should be revisited in the circular economy. 'Waste' means any substance or object which the holder discards or intends or is required to discard (EU Waste Framework Directive, 2008-2018). Waste has a legal status which aims to avoid the risks for the environment and public health if it is abandoned. The definition is based on the act of discarding, rather than the value of the material (Johansson and Forsgren, 2020). The main aim of waste management besides waste evasion should be today turning wastes to non-wastes (Pongrácz, 2002; Pongrácz and Pohjola, 2004). It is understood today that the primary objective of waste legislation is to control the fate of waste to achieve a high level of protection of human and the environment (Johannson, 2022) so that, with a toxicological and ecotoxicological formulation, the exposure of these targets to wastes contaminants is avoided and the hazard does not produce a risk.

This is meaningful in linear economy. In the linear economy, landfilling and even worse littering with the spreading of contaminants was the natural fate of waste, and an extensive regulatory system is needed to keep (mobile) contaminants tight in landfills, after eventual incineration, to avoid human and environmental exposure to contaminants of the waste. The material must be managed by its hazardous properties and the waste regulations (Hennebert, 2022b).

In circular economy, waste is disposed of in collection systems and treated in controlled modern industrial loops, so that no human and environmental exposure occurs. Only a small fraction of the material is unused and becomes waste. Accordingly, "... an object should only be considered waste, i.e. make waste legislation applicable, where necessary to protect human health and the environment. Conversely, objects that can be used safely without governance in the form of waste legislation should be considered something else" (Johannson, 2022). This author asks to "keep it simple". Other authors proposed previously a status of "certified material" (Johansson and Forsgren, 2020). In fact, the material is managed by the occupational safety and health regulations and industrial regulations during the processing, and by the products regulations during its second life. The specific demanding regulatory requirements for collection, grouping and transport of hazardous waste are shaped to minimise risk to human health and the environment, namely abandonment in the natural environment. Hazardous waste management by risk is proposed by Bodar et al. (2018). Waste could be treated by risk as products, according to REACH. Applications in which secondary materials including a certain content of critical compounds can be used safely should be developed (Friege et al. 2021). The interface between chemicals legislation and waste legislation should be as close as possible to achieve a circular economy (Friege et al., 2022; Hennebert, 2022b). In our opinion, the simplest thing is that, as soon as it enters the loop of modern collection and recycling, the material is managed like any raw material, and benefits from the status of end of waste. Another option is to create a new status for "secondary raw materials" in the European waste legislation to move away from the stark dichotomy between "waste" and "products" status for processed waste meeting industry specifications or quality standards, without prejudice to existing end-of-waste criteria, to level the playing field with primary materials, both in terms of regulatory constraints and public perception (EURIC, 2019).

4. CONCLUSIONS

This paper proposes, rather than lists of dangerous additives (hazard approach only), a risk approach: detecting the additives which make the plastic dangerous at their functional concentration and managing these plastics in controlled industrial loops (risk approach) so that the probability of exposure to hazards is very low, together with the phasing out substances of concern at the design stage.

Of 91 mineral and organo-mineral additives assessed in this paper, 34 additives make plastic hazardous. There are mainly heat stabilisers (10), pigments agents (9) and flame retardants (6). Two additives are under assessment by ECHA. For 24 additives, the polymers in which they are used is known. These substances should be further investigated in plastic loops. With the data of three previous papers on brominated flame retardants, other flame retardants and plasticisers, 63 additives (= 27% of 233) make plastic hazardous. The brominated flame retardants are the less documented. Only essential use should be allowed for pigments.

The sorting of the plastics with mineral and organo-mineral additives with minimal detectable concentration by online XRF could use Al, Co, Cr, Cu, I, Mn, Pb, V and Zn concentrations that are present in 32 additives making plastic hazardous at their maximal functional concentrations. The sorting of these plastics by the mineral concentration of their additives is therefore theoretically achievable.

EU waste regulation is designed to avoid human and environmental exposure to contaminants. That exposure occurs typically in linear economy by littering and secondarily by incorrect landfilling. Waste has a legal status which aims to avoid the risks for the environment and public health if it is abandoned. The definition is based on the act of discarding, rather than the value of the material. The main aim of waste management besides waste leaks should be today turning wastes to non-wastes.

In the circular economy, waste is collected in modern systems and treated in controlled industrial loops, so that there is virtually no human and environmental exposure (the probability of exposure to the hazard, i.e. the risk, is very weak). With occupational safety and health regulations and industrial regulations during processing, and with product regulations during its second life, the material must be managed as another hazardous or non-hazardous raw material (virgin), and benefit of the end-of-waste status as it enters the loop.

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