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Review

Automotive Paint Sludge: A Review of Pretreatments and Recovery Options

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Abstract: Automotive paint sludge (PS) is the waste product generated in the painting process of vehicle bodies. Although automotive spray painting is an automated operation, its efficiency is still quite low, since approximately 40–50% of the employed paint does not reach the target and, after being mixed with the collecting water, becomes PS. PS is a very complex material that contains several organic and inorganic components, in addition to 90% water immediately after production. Italian automotive factories produce from 2.5 to 5.0 kg of PS per painted car. If that figure is related to the number of vehicles produced worldwide every year, in the order of 100 million, it determines an annual PS amount in the order of 200,000–500,000 t. Consequently, a proper final destination for PS must be found. The waste management hierarchy and the principles of the circular economy require that we privilege solutions that foresee the recovery of valuable products or energy. This paper first reviews the processes and the machines that have been recently developed to obtain an enhanced mechanical dewatering of PS. The pretreatment of PS dewatering is often crucial in order to obtain high efficiency in the subsequent recovery process. Afterwards, the paper presents and discusses the recovery options that have been proposed and tested, at different scales, by several authors in the last thirty years. The processes for PS management can be grouped as follows: (i) direct employment of physically/chemically treated PS in the production of primers and sealants; (ii) utilization of PS for the production of building materials, as supplementary components of cement concrete, mortar, or bituminous mixtures; (iii) extraction of valuable organic and inorganic products by using thermal processes (pyrolysis, gasification); (iv) biological processes for PS detoxification, metal recovery, and stabilization before landfilling.

Keywords: automotive paint sludge; circular economy; cement concrete; hot mixture asphalt; pyrolysis; composting; adsorbents; dewatering; SDG-9: industry, innovation and infrastructure

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1. Introduction

Automotive paint sludge (PS) is the waste product that results from the industrial spray painting of workpieces and vehicle bodies. This operation, which occurs between welding and assembly, is composed of two main steps. Firstly, the vehicle body is protected from corrosion by means of degreasing, phosphate treatments, and electro-coating. Secondly, desired appearance, quality, and color are achieved by applying primers and top coatings [1]. Primers improve the resistance to stone chips and promote the adhesion of the top coat to the underlying electro-coat, thus preventing delamination. Nowadays, three main technologies exist for the preparation of primers. The technique initially adopted in the automotive field entailed the use of solvent-based products, in which resins, pigments, and additives were combined with relevant quantities of solvents. However, the need to reduce solvent-related gaseous emissions led to the development of alternative materials, the so-called water-based and powder primers [1].

The top coating applied on the primer layer is composed of a basecoat and a clearcoat. Basecoat, being a dispersion of organic and/or inorganic pigments in a liquid matrix, determines the body color. Clearcoat is a glossy, transparent layer that protects the basecoat from UV damage and guarantees durability and shine. As in the case of primers, both basecoats and clearcoats can be solvent-based, water-based, or powdered [2]. Nowadays, despite the fact that solvent-based products are still used in the majority of painting operations, the eco-friendlier water-based technology is spreading all over the world, especially in Europe. On the contrary, powder-based solutions are more common in the USA [1].

The painting operation of vehicle bodies at large automobile factories is generally carried out in a series of cabins called paint spray booths (Figure 1a). Although automotive spray painting is an automated operation, its efficiency is still quite low, since approximately 40% to 50% of the employed paint escapes into the surrounding air in the form of a mist, not reaching the target [3]. The excess paint mist is called "overspray". Such an overspray is typically collected by means of a water curtain or wet scrubbing, and the resulting fluid is thereafter collected through the floor grating beneath the paint booth. The mixture of water and paint compounds is conveyed using suction systems to appropriate reservoirs, namely sludge pits, and processed for water recovery [4]. Paint overspray and the residual water, which remains after water recovery, are usually referred to as PS (Figure 1b).

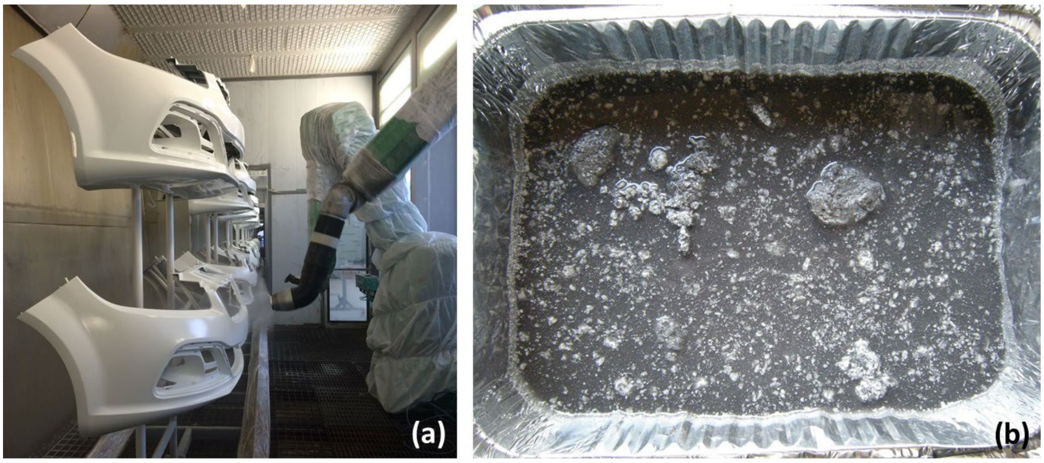

Figure 1. (**a**) Painting operations of vehicle parts (credit G. Salihoğlu); (**b**) automotive PS (credit B. Ruffino).

Italian automotive factories produce from 2.5 to 5.0 kg of PS per painted car [5]. If that figure is referred to the number of vehicles produced worldwide every year, in the order of 100 million, it determines an annual PS amount of 200,000–500,000 t, for which a proper final destination must be found.

PS is a very complex material, the exact composition of which depends on the type of paint used. The main components of PS are water and organic solvents, in addition to a variety of paint ingredients, including uncured polymer resins, curing agents, pigments, surfactants, and other minor formulation constituents [6]. The presence of uncured paint resins, which cure and form a film upon heating, makes PS very sticky and difficult to handle. Therefore, detackification agents are often added to the sludge for easier management of PS [7].

Some years ago (2016), Salihoglu and Salihoglu [4] published a comprehensive review concerning the PS coming from the automotive industry. In the first part of their work, they provided a detailed description of the environmental aspects of an automobile manufacturer. Subsequently, with the aid of mass balances, they demonstrated that the primary source of hazardous waste at an automotive factory can be attributed to a single unit operation, namely automotive painting. They treated the aspects that concerned the generation and composition of PS with great detail, and, finally, they devoted the last section of their review to the management of PS. Some years after the work of Salihoglu and Salihoglu [4], this work intends to expand and complete the literature review provided by the two authors, with a specific focus on the processes developed from the Nineties to the present day that aim not only to reduce the hazardousness of PS but, in line with the waste hierarchy and circular economy principles, to transform PS into valuable products and energy. To the best of our knowledge, there are no other review papers treating this subject. The management of PS has to be deemed a hot topic because of the growing demand for passenger cars that most of the European countries have recorded over the last 30 years [8], as shown in Figure 2.

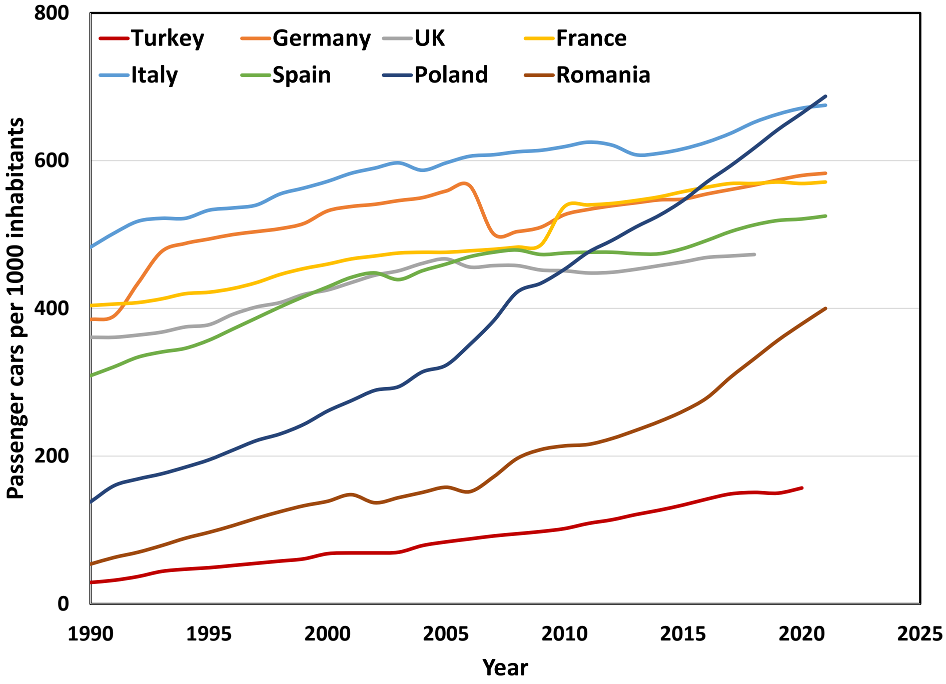

Figure 2. Trend of passenger cars per 1000 inhabitants in the biggest European countries (1990–2021) [8].

The literature review that formed the basis of this paper was carried out through the consultation of research papers and patents. As reported in the subsequent sections, the recovery options for automotive PS can be grouped as follows:

- employment of physically/chemically treated PS in the production of primers and sealants.
- Utilization of PS for the production of building materials as supplementary components of cement concrete, mortar, or bituminous mixtures.
- Extraction of valuable organic and inorganic products by thermal processes (pyrolysis, gasification).
- Biological or chemical stabilization before disposal.
- Other solutions.

The two initial sections of this review paper are devoted to providing (i) a characterization of PS based on the data from the studies considered in this work and (ii) an overview of the methods and machines utilized to dewater and dry PS before utilization. In fact, most of the above-mentioned solutions for PS recovery require a material with a reduced content of water or in the form of a dry powder.

2. PS Characterization

PS that originated from the application of basecoat were considered the most interesting by-product, for both quality and quantity, in the view of a recovery process. Almost all studies included in this review paper used basecoat PS to test processes intended for sludge valorization. Table 1 reports the results of the characterization of some PS samples. It can be seen that the analyzed parameters differ from one study to another, depending on the specific focus of the research. Studies aimed to employ PS as supplementary components of building or infrastructure materials after undergoing physical and/or chemical treatments, privileging parameters such as metal content [9–12]. For thermal valorization, the parameters that were deemed more useful were the contents of water, organic matter, and ashes, together with heating value [13]. Finally, the characterization propaedeutic to PS stabilization through biological processes included the assessment of organic matter, macro-nutrients (i.e., nitrogen, phosphorous, sulfur), micro-nutrients (i.e., boron, copper, iron, manganese, zinc), and non-essential or inhibitory inorganic and organic substances (i.e., arsenic, cadmium, lead, nickel, BTEX) [14,15]. In some cases, metals were not determined on the PS sample (or on its ashes), but on the liquid phase obtained from a leaching test, carried out, for example, according to EN 12457 standard procedure [16].

Data from Table 1 highlight a high variability in the water content due to the relevant heterogeneity of production processes and PS management operations carried out in different automotive plants. The water content was, on average, in the order of 60%. That value indicated that PS, before sampling, underwent dewatering processes performed with filter presses or centrifuges (see Section 3). In one case [13], the PS sample was characterized immediately before the tests were carried out for its valorization, and the water content showed a very low value. The water content is considered an important energy parameter required for drying processes. For this reason, it seems crucial for the automotive companies to try to reduce the water content in the dewatering phase by homogenizing their production processes as much as possible and by using proper devices.

PS had, on the basis of the considered studies, a quite high content of organic matter. It can be seen from Table 1 that the samples of basecoat PS analyzed by different authors had a similar value of organic matter content, in the order of 75% on a dry basis (d.b.). According to the data reported in a previous study carried out by the Politecnico di Torino research group [17], the organic substance in a sample of clearcoat PS was approx. 95%. Such high values of organic matter content make PS, especially the type coming from clearcoat application, a promising material to be used as a substitute for some ingredients in primer or sealant production, as a supplement to neat bitumen for the production of modified binders to be used for hot mixture asphalt (HMA), or, finally, to undergo composting processes.

The average heating value was between 4000 and 6000 kcal/kg. This value is of the same order as that of materials, like wood, ordinarily used in thermal processes. Consequently, PS can also be considered for other alternative applications, such as auxiliary fuel in cement plants. Despite the variability among painting processes, a difference between basecoat and clearcoat was evident when PS were analyzed in terms of chromium, cobalt, copper, and titanium. Basecoat PS showed values up to two orders of magnitude higher than those of clearcoat, probably due to the presence of those metals in the colored pigments of basecoat paints [17].

Table 1. Results of the characterization of PS samples.

Parameter	Gautam et al., 2010 [9]	Januri et al., 2015 [13]	Tian et al., 2015 [14]	Dalmazzo et al., 2017 WB [17]	Dalmazzo et al., 2017 C [17]	Salihoglu et al., 2018 [15]	Yenikaya et al., 2018 [16]	Gadhekar et al., 2019 [10]	Abu Bakar et al., 2022 [11]	Yeganeh et al., 2022 [12]
Water content (%)	29.9	2.4	NA	50.9	60.8	63.4	63.4	54.5	29.9	70.65
Organic matter or VS (%, d.b.)	75.2	75.9	NA	72.4	94.5	72.6	NA	75.66	75.2	NA
Ash (%, d.b.)	22.7	2.9	NA	27.6	5.5	NA	NA	24.83	22.7	NA
Fixed carbon (%, d.b.)	2.1	3.2	NA	NA	NA	NA	NA	NA	2.1	NA
Heating value (kcal/kg)	4330	22.6 (MJ/kg)	NA	4280	4820	7682 (kJ/kg)	NA	5705	NA	NA
Loss on ignition (%)	0.2	NA	NA	NA	NA	NA	71.0	NA	NA	NA
Fe (%)	6.2 (Fe_2O_3)	NA	0.16	0.268	0.08	NA	NA	0.025 (mg/L?)	6.6	0.43 (Fe_2O_3)
Al (%)	18.0 (Al_2O_3)	NA	2.26	2.42	1.02	NA	NA	NA	19.1	18.0 (Al_2O_3)
Ti (%)	53.0 (TiO_2)	NA	NA	6.81	0.0044	NA	NA	NA	56.2	54.2 (TiO_2)
Si (%)	6.8 (SiO_2)	NA	NA	NA	NA	NA	NA	NA	7.2	2.15 (SiO_2)
Ba (%)	8.5 (BaO)	NA	6210 (mg/kg)	6.57	41.7	NA	6.4 mg/kg (L)	NA	9.0	NA
P (%)	0.4 (P_2O_5)	NA	0.19 (g/kg)	NA	NA	NA	NA	NA	0.4	NA
Na (%)	0.2 (Na_2O)	NA	NA	NA	NA	NA	NA	NA	0.2	NA
K (%)	0.2 (K_2O)	NA	0.34 (g/kg)	NA	NA	NA	NA	NA	0.2	NA
Ca (%)	0.4 (CaO)	NA	1.28 (g/kg)	NA	NA	NA	NA	NA	0.4	2.30 (CaO)
Mg (%)	0.4 (MgO)	NA	2.02 (g/kg)	NA	NA	NA	NA	NA	0.4	0.66 (MgO)
Cl (%)	0.14	NA	NA	NA	NA	NA	440 mg/kg (L)	NA	0.14	NA
Co (mg/kg)	NA	NA	4.80	144	0.847	NA	NA	NA	NA	NA
Cr (mg/kg)	NA	NA	38.1	228	9.17	152.2	NA	ND	NA	106
Cu (mg/kg)	NA	NA	47.5	171	7.07	NA	<1 mg/kg (L)	ND	NA	NA
Ni (mg/kg)	NA	NA	42.4	18.3	5.21	10.7	<0.5 mg/kg (L)	0.19 mg/kg	ND	16.2
Pb (mg/kg)	NA	NA	< 0.003	17.0	9.85	10.5	NA	ND	NA	15.2
Zn (mg/kg)	NA	NA	28.1	172	186	NA	<1 mg/kg (L)	0.12 mg/kg	ND	NA
pH	NA	NA	NA	NA	NA	9.4	9.44	7.6	NA	NA

NA: not available; ND: not detected; WB: water-based; C: clearcoat; (L) analysis performed on the leachate from leaching test; d.b.: dry basis.

3. Pretreatment of PS: Dewatering and Drying

The water content of a PS affects the cost and convenience of sludge management. PS has an average water content, immediately after production, in the order of 90%, with a complementary total solid (TS) content of approx. 10% [1,2]. Mechanical dewatering processes carried out through filter presses or centrifuges can increase PS TS content from around 10% to 30–40%, which are acceptable values for further drying operations [2]. Some specific machines have been recently developed for an enhanced mechanical dewatering of municipal and industrial sludge and, specifically, PS.

Strizbox®, patented by the Italian Idee & Prodotti company (Patent number 0714318), is a sort of filter press that combines pressure and motion in an "active filtration" process, aimed at producing a dewatered cake [18]. The system consists of vertical columns with a maximum height of 6 m. Several columns can be installed side by side in order to obtain the necessary treatment capacity. Sludge is fed from the top, filling the column, and the dewatered sludge is discharged at the base. A cylindrical cake is formed thanks to the action of the membranes placed on the periphery of the tube and alternately air-inflated, which squeeze sludge under pressure and eject the liquid. Each meter of the filter tube produces 35 dm^3 of cake per cycle.

Drybox®, patented by the same company (Patent Numbers 22669A and 0714318), is a dewatering system set up in a rigid roll-off container that simultaneously uses gravity and the "active filtration" process to remove the liquid phase [18]. The tank has a volume of 20 m^3, with a total drainage area corresponding to the whole floor area. The container is supplied with either disposable or long-life filter cloths. The sludge is collected in the bag of filtering material placed inside the container. The bag with sludge is moved thanks to the expansion of wide-expansion membranes, which are placed in the lower part of the filter cloth. Membranes expand towards the sludge with an on-off movement, causing cracks in the sludge panel and facilitating water drainage. At the end of the dewatering process, the external rigid container is opened, and the bag with the dehydrated sludge is easily removed [16].

CentraSep S-Series centrifuges, manufactured by the Trucent company (Dexter, MI, USA), are vertically standing self-discharging machines built around a bottom-fed/bottom-discharge design, driven by a single top-mounted motor [19]. The precision-machined cast bowl and positive-locking clutch of the S-series prevent oscillation during operation, reducing wear and increasing efficiency. Centrifuges can separate the paint solids that originate from either side-draft (water curtain) or down-draft spray booths. The treated PS can originate from either water-based, solvent-based, or 2-component (epoxy) paints. The Trucent CentraSep centrifuge is often used in order to keep the process water clean [19].

Decanter centrifuges, manufactured by Flottweg (Germany) or by DolphinCentrifuge (Warren, MI, USA), have special wear protection adapted to PS processing [20,21]. The above-mentioned machines can dewater the incoming sludge so as to reduce its volume to 10% of the original volume. This reduces the amount of solid waste to be further managed and consequent operating costs. In order to increase dewatering performance, coagulants help to concentrate the paint particles. According to the manufacturers, decanter centrifuges require less coagulant than traditional centrifuges for the same solid discharge. The treated process water can be reused for the production process, thus resulting in the saving of a significant amount of fresh water.

Belt dryers were developed with the aim of drying various sludges to a final TS content of 65–95% in an energy-efficient and dust-free way [22]. The mechanically dewatered sludge is extruded onto the perforated belt, where it is conveyed slowly through the drying zone and discharged at the end of the conveyor. In order to obtain homogeneous drying, the retention time of the belt dryer can be adjusted very accurately. Evaporation rates range from 200 kg/h to 3000 kg/h [22].

The patented CENTRIDRY® (by Euroby, Sussex, UK) enhanced dewatering process combines mechanical dewatering and thermal drying in a unique machine [23]. The CENTRIDRY® system can process both municipal and industrial sludge, with an incoming TS content of 2–7%, and produces fine-grained or pelletized sludge with 60–90% TS in a few seconds. Liquid sludge first undergoes a mechanical dewatering stage in a modified CENTRIPRESS® centrifuge, preferably after being mixed with a polymer. The sludge needs to reach a minimum TS content of 25% in the dewatering stage before being treated in the centrifugal stage. Afterwards, the sludge is discharged into the thermal stage in the form of a fine-grained spray. The outer casing of the standard CENTRIPRESS® is replaced by an insulated cyclone jacket, which is fed by the high-speed sweep gas that comes from the hot gas generator. The particles of sludge that enter the cyclone chamber are instantly dried. In this way, the sludge does not stick to the walls when it makes initial contact with the external walls. The particles are instantly entrained and conveyed in the sweep gas and exit the jacket in a few seconds. During that time, the sludge granules are dried, and the temperature of the conveying gas is lowered. The operations of pneumatic conveying and drying continue during the transport time to the cyclone, where the product particles are separated and discharged via a rotary valve to the stockpile [23]. The sludge coming from the centrifugal dryer has a fine-grained structure. The mean diameter of the particles, in the order of 1 mm, depends on the type of sludge and on the degree of drying. The grain shape is not spherical, and the individual particles are characterized by a rough, coarse surface. Due to the way they are generated, the particles have a very large specific surface, with bulk densities ranging from 600 to 750 kg/m^3. The dewatered sludge product obtained with the CENTRIDRY® plant can be formed into pellets when the dry substance content is between 65% and 85%. Below a dry solid content of 65%, the pellet tends to cede; conversely, above 85%, it has a lower internal coherence, which increases the wear at the pelletizer and thus reduces the throughput. For the purposes of a fast and uniform incineration of the dried sludge, pelletizing the sludge is not necessary [23]. After the separation of the dewatered sludge, excess vapors are drawn off the system by a small blower. Exhaust vapors are first conveyed in a venturi scrubber in order to remove residual amounts of fine dust and volatile components and, subsequently, treated for odor abatement.

Sludge drying can also be obtained with either a microwave process or solar energy utilization. Yenikaya et al. tested a microwave drying process on samples of mechanically dewatered sewage sludge (SS) and water-based PS coming from a Turkish automotive plant [16]. They studied the effect of some parameters, namely the dielectric constant, sludge form (raw or ground), drying method (microwave and conventional), drying period, and air curing. They observed that the moisture loss after 10 min increased from approx. 3% in an electric oven to 30% in a microwave oven with a power output of 900 W. Air curing of the samples following drying in the microwave oven resulted in a small additional moisture loss, whereas sludge grinding did not show any effect on the dewatering process. The results of the study could contribute to establishing the necessary conditions for scaling up, but further research was necessary to demonstrate the effective technical and economic feasibility of the process.

Amin and Salihoglu applied solar drying to PS (with a water content of 56%) and compared its drying efficiency with that of SS (with a water content of 80%) [24]. An amount equal to 512 g of water was evaporated from one kilogram of PS, decreasing the water content from 56% to 4.8%, when 1671 $\mathrm{Wh/m^2}$ of internal cumulative solar radiation was provided by the solar dryer. The researchers found that, although the initial amount of moisture in the SS was higher, the rate of evaporation in the PS was much higher in the first hours of solar drying. This phenomenon was associated with a higher amount of free water in the PS than in the SS. After the free water of the PS was evaporated, a thin and hard layer was formed as an external coating of the sticky PS. The researchers noted that the presence of solvents and pigments in the PS complicated the evaporation process since the heat could not enter the PS [24]. The same group of researchers improved the drying of PS with some modifications to the solar drying process by distributing steel screws on the sludge tray, covering the system floor with a black trash bag, and mounting the reflector around the absorber [25]. They concluded that the PS absorbed heat through the tray and screws by the conductive method; therefore, the drying rate increased. The black coating of the dryer floor led to the complete absorption of the solar radiation, and the reflector enriched the sunlight to increase the internal temperature in the dryer. Amin et al. gave the details of the solar drying system containing paraffin as a phase change material that was designed to dry PS and suggested solar drying as an alternative step in PS management before recovery [26].

4. Recovery of PS in the Paint or Sealant Industry

Patent WO 2007 072502, in agreement with the principles of the circular economy, presents a process aimed to convert PS into a reusable paint [27]. According to the inventors, several kinds of PS could be suitable for the recycling process, namely amino-alkyd-based, epoxy, acrylic-based, polyester melamine-based, amino polyester-based, thermosetting acrylic, urea-based, silicone or modified silicone-based, and acrylated alkyd PS.

As shown in Figure 3, the process for the production of new paint from PS started with a rinse of the wet sludge with water. PS was subsequently mixed with a solution of either sodium bicarbonate ($NaHCO_3$, 3–10% b.w. of the PS), if the booth additive was acidic, or paratoluene sulfonic acid (PTSA, 0.2–0.5%), if the booth additive was alkaline. After a subsequent rinse with methyl alcohol, the residual liquid phase, which wetted the sludge, was removed with pressing, centrifugation, or mild heating. The complete removal of the liquid phase was obtained with a drying operation carried out at a temperature range from 35 to 75 °C (or at room temperature) for a period between 1 and 72 h, depending on the sludge condition and quality.

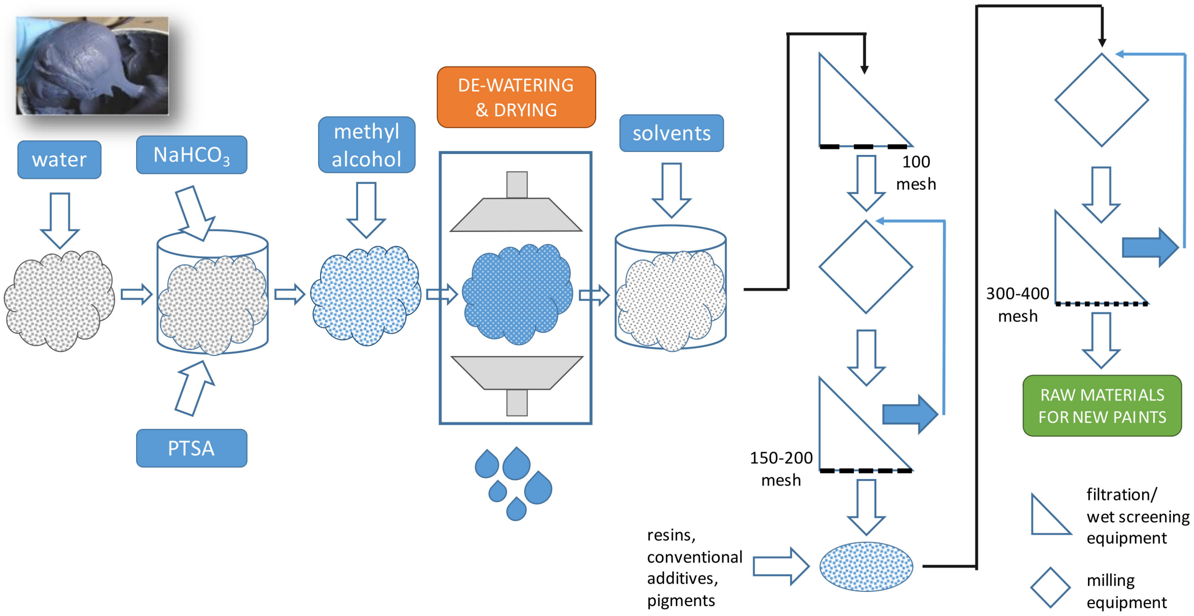

Figure 3. Scheme of the recycling process [27] aimed at converting PS into a reusable paint.

The dried sludge was soaked in one or more solvents (this information was not disclosed by the patent), depending on the type of PS used as a raw material, and subsequently stirred in order to obtain a homogeneous mixture. Recommended durations for the two above-mentioned operations were 1–48 h for soaking and 0.5–4 h for stirring. The obtained mixture was subsequently subjected to a series of sequential operations of milling and wet screening (or filtration), as shown in Figure 3. The first and second milling operations were aimed at reducing the filtrate product to sizes of +2 (100 mesh) to +3 (150–200 mesh) and +6 (300–400 mesh) Hegman's Gauge fineness, respectively. Particles retained in each filtration step were recycled back for reduction to smaller sizes by conventional pulverizing equipment. The filtrate product, after filtration at 150–200 mesh, could be added with one or more resins, conventional additives, and pigments, if necessary. Particles with dimensions less than 300–400 mesh were finally suitable to be used as raw materials for the preparation of new paints. The conversion of PS into a reusable paint required several additives, individually or in combination. The choice of the most suitable additive depended on the type of PS. Pigments must also be added in order to achieve the desired color [27].

To the best of our knowledge, the process patented by Bhatia et al. [26] was the only one capable of transforming the waste paint into the same original product or an ingredient of it. However, no applications of such a process were found on an industrial scale. Obstacles to the industrialization of the recycling process were (i) the need to know the exact composition of the paint used in the painting operation, which determines the choice of the reagents necessary for the recovery process; (ii) the inapplicability of the recycling process in the case of a mixed (or contaminated) PS; and (iii) the number of reagents and unit operations required by the recycling process.

Active principles of organic nature contained in PS, namely uncured resins and hydrocarbons, were deemed of interest for the production of sealants. US Patent N° 4,980,030 protected the first process aimed at recovering PS as a filler in the formulation of sealing products [28]. The painting waste, typically in the form of sludge, was processed with a procedure that included the operations of heating and resin curing. Water and volatile organic compounds (VOCs), in the form of liquid hydrocarbons, were evaporated so that the product, discharged after heating, was in a dried particulate form. The heating operation was also aimed at curing the uncured polymeric paint resins. The inventors recognized three main benefits to the patented process:

1. It reduced the final volume of the waste and made its disposal easier and more economical.
2. The power produced can be handled easier than wet sludge.
3. It reduced the hazardousness of the waste because liquid hydrocarbons were evaporated and toxic metals were bound into the cured resin product.

A similar process was reported in US Patent 5,087,375 [29], which disclosed a method to heat and calcine PS in order to produce a powder that could be used as a filler for sealants. It has to be underlined that the processes reported in both the afore-mentioned patents [28,29] completely cured any uncured polymers during the heating and/or calcining step. Accordingly, the resulting product was an inert, inorganic, brittle, and abrasive particulate material. An improved process, in which the heating temperature did not exceed 38 °C, was presented in US Patent 5,254,263 [7]. In the presence of such a low temperature, polymer resins remained uncured, and, according to the inventors, the resulting product was soft and easily dispersible as a filler in sealants' compositions.

However, fillers are not the sole components of sealants, which generally also include other ingredients such as polymers and plasticizers. These components typically account for up to 75% of the overall composition of the sealant, and polymers, in particular, are the principal cost item in the sealant's formulation. For this reason, it was deemed of interest to test the capability of PS to be used as a replacement for one of the polymeric components in sealants in order to reduce production costs.

US Patents 5,880,218 [30], 5,922,834 [31], and 6,455,598 B1 [32] describe a process in which the uncured polymers contained in the treated PS could be used as a partial replacement of the polymeric components in the formulation of products like heat-curable sealants, pressure-sensitive sealants, caulking sealants, and automotive paintable seam sealers. The process was articulated in the three phases of drying, de-catalysis, and powder production through the addition of processing fillers, as shown in Figure 4.

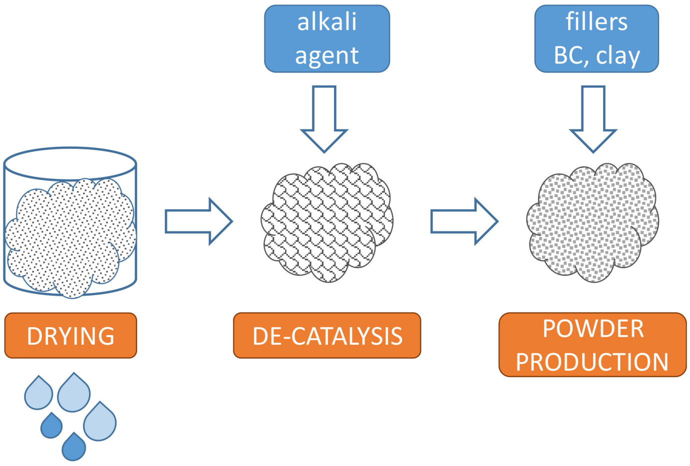

Figure 4. Scheme of the recycling process [30–32] aimed at converting PS into ingredients for the production of sealants.

The phase of drying had to be preferably carried out by agitating the raw sludge under vacuum at a temperature of approx. 110 °C. These operating conditions determined the removal of a substantial amount of water and low-boiling solvents from the PS, thus leaving the polymers uncured. In the second phase, PS underwent a treatment of de-catalysis with an alkali agent (which was selected from di-ethanolamine, 2-amino-2-methyl-2-propanol, di-isopropanol amine, tri-isopropanol amine, potassium hydroxide (KOH), and sodium hydroxide (NaOH)) capable of guaranteeing a pH ranging from 8 to 13. The dose of the added alkali agent ranged from 0.1% to 10% of the PS's dry weight. In the de-catalysis phase, the catalyst contained in the PS was neutralized so that the curing component was not activated upon heating. In the presence of a solvent-based PS containing polyester, acrylic, and melamine resins, the above-described process produced a putty. Finally, in the third phase, putties were converted into powders by the addition of 5–75% b.w. of processing fillers, namely black carbon (BC), clay, or a mixture thereof.

Furthermore, in this case, the success of recycling PS in the production process of sealants seems to be dependent on both the correct choice of the reagent to be used for the de-catalysis operation and the homogeneity of the waste in terms of composition. These requirements, together with the costs of reagents, had a strong impact on limiting its industrialization.

5. Recovery in Building Materials

Another field that was deemed promising for accommodating PS was that of building materials. Investigations have been carried out in order to explore the possibility of employing PS as a supplementary component of Portland cement concrete, lightweight construction mortar, and bituminous mixtures for paving applications.

5.1. Recovery in Portland Cement Concrete

Cement concretes contain inert aggregates, a binder, water, and, eventually, additives. Studies were carried out to test the capacity of PS to replace either the binder or the water used for the mixture. In both cases, in order not to damage the properties of the concrete or cement paste incorporating PS, it is necessary that PS does not react with the other components of the mixture.

In the mid-1990s, St. Louis patented a process aimed at recycling PS into building materials, the main step of which was the stabilization of any aluminum contained in PS [33]. According to the inventor, aluminum could adversely impact the performance of the cement produced through the admixture with PS. As shown in Section 2, PS generated from water-based basecoat paints contains 2–2.5% b.w. of aluminum. Free aluminum, typically aluminum flakes, is commonly used in automotive paint to obtain greater reflectivity or shininess.

The process for aluminum inertization included four steps, as shown in Figure 5:

1. Mixing PS with NaOH so as to chemically stabilize the free aluminum contained in the sludge.
2. Heating the PS-NaOH admixture to a temperature of approx. 60 °C for 10 min, so as to facilitate hydrogen generation from the reaction between free aluminum and NaOH.
3. Mixing the PS-NaOH admixture with quicklime (CaO), so as to absorb the residual water within the PS.
4. Agitating the obtained admixture so as to minimize any localized heterogeneity.

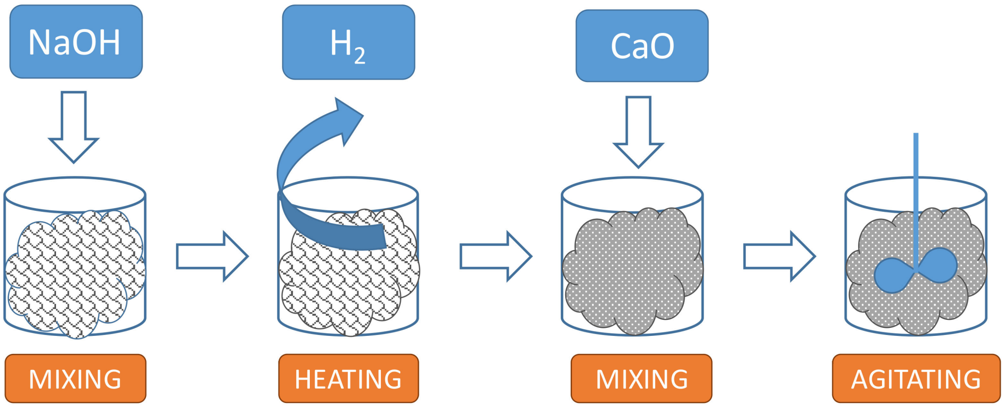

Figure 5. Scheme of the recycling process [33] aimed at producing building materials from PS.

The patented process was optimized for PS containing 50% TS, but the process could be applied to PS with TS contents ranging from 30% to almost 100%. Whether the TS content was less than 30%, PS could be further concentrated with a dewatering process.

Powdered NaOH was deemed the preferred agent for pre-treating PS because:

- It does not alter the mechanical properties of the solid lime/paint product.
- It is of proven efficacy, inexpensive, and readily available.
- It generates sufficient heat upon dissolution into the PS to facilitate the reaction with free aluminum.

The first mixing step preferably required NaOH at approximately 1.0 M concentration, although concentrations from 0.2 M to 0.5 M were also acceptable. The range of concentrations was proportional to the amount of aluminum within the PS. Ideally, the process required an amount of NaOH just enough to reduce all the free aluminum into the PS.

The heating step of the PS-NaOH mixture was inherent in the case of mixing powdered NaOH. However, if an aqueous NaOH solution is used, heat should be provided by another source. The heating step facilitated the reaction between NaOH and the free aluminum in the PS, thus causing the formation of hydrogen bubbles. This pretreatment prevented any subsequent "bulging" problems with the resulting cement product and was believed to avoid weakening the structure where cement was employed.

The third step of the process was ideally performed by adding approx. 1.6 kg of CaO for each kilogram of PS. This ratio was assumed to be optimal as the water content in the PS was approx. 50% b.w. The ratio between the molecular weights of CaO (56 g/mol) and water (18 g/mol) requires approx. 3.1 kg of CaO to react completely with 1 kg of water. CaO mixes with the water contained in the PS in a highly exothermic reaction.

The process presented in Patent 5,573,587 resulted in a 75%/25% hydrated lime $Ca(OH)_2$/solid paint mixture and included a final step of agitation/stirring aimed at minimizing any localized concentrations of paint solids [33]. Agitation was produced mechanically, through standard plow-paddle or pug mill mixers. Agitation further ensured an efficient mixing of the CaO with the raw PS, thus rapidly eliminating any unpleasant odor produced by the raw PS.

The employment of PS as a supplementary component of Portland cement concrete was deemed to provide beneficial effects in limiting concrete shrinkage [34,35]. Susceptibility to tensile cracking, which occurs when volume contractions associated with drying shrinkage are wholly or partially restrained, is one of the major disadvantages of Portland cement concrete. In order to overcome this obstacle, a number of additives, based on the formation of ettringite (hexacalcium aluminate trisulfate hydrate, $(CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O$) during the first days of concrete curing, have been developed over the last 50 years. Ettringite can attract a large number of water molecules, which cause inter-particle repulsion and thus produce an overall expansion of the system. The potential expansion produced by ettringite formation is controlled by the use of ordinary steel reinforcement. The development of inexpensive expansive additives could make the use of shrinkage-compensating concrete more widespread.

PS was deemed worthy of interest for producing shrinkage-compensating concrete because the paints used in the automotive industry incorporate various calcium compounds. These calcium compounds, used as fillers or bulking agents, are consequently found in PS. The calcium content of PS, which originates from both basecoat and clearcoat, was in the order of 1% b.w. dry basis (9.67 g/kg for clearcoat, 11.4 g/kg for basecoat) [36]. The process for recycling PS as a reactive expansion additive required the removal of volatile compounds through a drying operation carried out at temperatures ranging from 100 °C to 400 °C, preferably using a screw retort apparatus. The so-called expansion additive can contain water or other liquids, so long as they do not interfere with the curing of concrete. The dried PS had to be milled so that the powder particles had a particle size distribution between 74 µm and 850 µm. Particles were finally dispersed into the cement in an amount between 0.5 and 5% b.w. of the cement. Desirable expansion properties could be obtained at an amount of PS powder-to-cement of approx. 5% b.w., although for most applications, amounts of 1 to 2% b.w. were preferred [34]. Larger amounts of PS caused the concrete to crack at the surface. The expansion properties of Portland cement concretes incorporating powdered PS were comparable to those obtained with some purpose-made expansion additives. The presence of PS powder did not adversely influence the concrete's resistance to chemical and physical causes of deterioration, particularly sulfate attack. The environmental impacts of using the PS powder in concrete were deemed negligible.

The above-mentioned processes were patented between the late 1990s and early 2000s; however, also recent studies have tested the feasibility of replacing an amount of cement with PS for the production of concrete or cement-based composites. Specifically, Ahmad et al. [37] investigated the mechanical and durability properties of cement pastes prepared with cement replacements of 5–30% with PS. They reported an unconfined compressive strength (UCS) increase for 5% PS replacement but a decrease with higher PS doses. They attributed the higher UCS observed in the 5% PS-incorporated sample, compared to that of the control, to secondary C-S-H gel formation resulting from the pozzolanic action of PS. Furthermore, they observed that an addition of PS inhibited ettringite crystal formation in the cement-mortar matrix, contributing to less expansion and enhanced mortar performance under sulfate attacks. That was due to the fact that, in the considered PS, the alumina content was low whereas the silica content was high.

Feng et al. [38] added doses of polyurethane-based PS ranging from 0 to 20% b.w. of the cement employed for concrete production. Tests performed to assess the compressive and flexural strengths of specimens revealed that the addition of doses below 10% improved both properties. Conversely, Yeganeh and Khatamgooya [12] observed a general decrease in both the compressive and flexural strengths of cement concrete samples in which amounts from 5% to 20% of cement were replaced by PS. The highest values of the two properties were found for a PS dose of 10% in the mix design with a target compressive strength, in the non-modified sample, of 30 MPa. However, even such values were deemed insufficient (65% of the value for the non-modified sample for compressive strength and 90% for flexural strength) to use the PS-modified cement concrete for construction purposes. Furthermore, the two authors observed that the presence of PS caused a decrease in workability due to pozzolanic reactions and that the presence of organic substances negatively affected the continuity of the concrete structure.

Abu Bakar et al. [11] reached similar conclusions by testing a batch of PS collected from a manufacturing company in Malaysia to produce PS-modified cement paste. PS were preliminary dried, milled in a ball mill for size reduction to <9 μm, and characterized through fourier transform-infrared spectroscopy (FTIR), X-ray diffraction (XRD), and X-ray fluorescence spectroscopy (XRF). Control samples of composite cement paste were prepared by mixing cement, water, and a high-range water reducer (HRWR) according to a 100:20:1.5 b.w. ratio. The HRWR was added to the formulation in order to control the workability of the fresh cement paste at the low water amount used in the mix. PS was added to replace 1, 3, 5, 7, and 10% b.w. of cement. According to the authors, metal oxides, i.e., Fe_2O_3, contained in PS could be capable of increasing mechanical strength and expediting the cement hydration process. However, the values of compressive strength registered at days 3 and 7 of early-stage curing aging were lower in the samples with PS replacement than in the control. That worsened behavior was attributed to the probable formation of a weak interfacial transition between PS and cement paste and to a higher total and capillary porosity. The authors concluded that further investigations were necessary to improve the quality and characteristics of the PS-added composite.

Tests were also carried out to verify the capacity of PS to be used directly in its liquid state as a partial substitution for water. The process presented in US Patent 7,128,780 [35] included two subsequent steps:

(1) Mixing liquid PS with one or more materials used to produce building materials, such as cement mix or concrete mix, or portions thereof.
(2) Allowing the mixture to cure, thereby producing a building material.

Preferably, PS was the sole source of hydrating material. Optionally, additional water could be added to provide the desired amount of water to the building material.

Burande [39] suggested replacing water with liquid PS for the production of concrete, but the paper did not report the water content of PS and provided only limited details on the methods used for the execution of the tests. The results obtained by the author showed that traditional concrete and concrete containing PS had comparable stresses and strains that were well below the ASTM requirements. Conversely, Salihoglu and Salihoglu [40] came to a different result by investigating the influence of using water-based PS as a replacement for mixing water on the unconfined compressive strengths (UCS) of Portland cement paste and concrete samples. PS was used after being diluted to a residual dry-solids content of 10%. Salihoglu and Salihoglu [40] also prepared geopolymer samples by using sodium silicate and NaOH solutions as an activator and low-calcium fly ash (ASTM Class F) as an aluminosilicates agent and geopolymer precursor. They found that geopolymer samples resulted in higher UCS levels compared to Portland cement samples. However, they observed that the presence of diluted PS in the samples influenced the UCS levels adversely. For example, the UCS of Portland cement concrete decreased from 18 MPa to 5 MPa when the diluted PS was used as a water replacement. Similarly, the introduction of diluted PS into geopolymers determined a 50% decrease in UCS (from 32 MPa to 16 MPa). In order to obtain better results in UCS of concrete and geopolymer samples, the dilution level of PS should be increased, whether PS wants to be used as a water replacement.

The above-reported experiences demonstrated that the original content of calcium in PS, or that added to obtain aluminum inertization, could make PS a good candidate to be used as an additive for limiting concrete shrinkage. Shrinkage-compensating concrete incorporating PS could find particular application in parking structures, in order to prevent water leaks that can cause damage to cars, or in bridge deck overlays, where it helps to minimize cracking and control the corrosion of steel in the bridge deck [34]. However, as observed by Ahmad et al. [37], the composition of PS affected the potential for ettringite formation and the behavior of the concrete/composite toward sulfate attack. The results of the reported studies show a general agreement concerning the fact that the replacement of up to 10% of cement with PS could improve (or, in any case, not adversely affect) the performance of the concrete. However, it has to be considered that the different compositions of the traditional binder used in concrete (i.e., cement) and PS might create discontinuities at the interface between the two substances, with a consequent reduction in the paste strength.

5.2. Recovery in Lightweight Construction Mortars

Sludge generated from the painting of white goods was used to replace sand or lime in the production of mortars [41]. The study by Avci et al. [41] used a dry PS that resulted from the mixture of three paint products (a zinc yellow primer, a metallic gray topcoat, and a solvent-based clearcoat). In the first part of the study, PS was used to replace an aliquot of sand in the composition of the standard mortar mixture, thus obtaining PS to cement ratios from 6% to 30%. In the second part of the study, PS was used to replace up to 30% of lime. All the tested specimens showed an unexpected expansion capacity compared with the reference mortar at fixed curing periods. Higher expansion and porous content could guarantee better thermal and insulating properties. Expansion could be due to the polymers and calcium-based materials contained in the PS, which act as fillers or bulking agents and can attract a large number of water molecules, thus determining inter-particle repulsion. However, adding PS to either cement (PS-cement) or lime (PS-lime) resulted in a decrease in strength. The authors concluded that the overall properties of the PS-modified concrete products made them of interest for use as lightweight residential construction materials.

5.3. Recovery in Bituminous Mixture for Paving Applications

In 1998, Martínez-González et al. [42] developed a process that used automotive PS to improve the stability of asphalt mixtures. PS were initially dried with hot air at a temperature of 180–230 °C. Subsequently, PS was mixed with inerts and binders to prepare three dry asphalt mixtures. The three mixtures contained (i) basaltic rock with asphaltic emulsion, (ii) tezontle rock with asphaltic emulsion, and (iii) forged rapid asphalt with tezontle rock. In all cases, the amount of binder was 6% of the mixture, and PS substituted amounts from 0 to 6% of inerts. Stability and environmental compatibility of the mixtures were tested with the Marshall stability test, and a leaching test that was carried out according to Mexican Regulation NOM-053-ECOL-1993, respectively. It was seen that the addition of automotive PS increased the average Marshall stability value of the mixtures. The concentration of chromium extracted from the tested samples was below the maximum value allowed by the Mexican regulation.

The research group from Politecnico di Torino carried out a comprehensive evaluation of the utilization of automotive PS for the production of bituminous binders for paving applications [17,43,44]. Water-based basecoat and clearcoat sludge were dried and milled to obtain a fine powder to be mixed with two neat bitumens with different chemical compositions. Sludge was added in doses of 10% and 20% b.w. of the neat bitumen. The rheological and performance-related properties (i.e., performance grade (PG) according to the SUPERPAVE scheme) of the so-obtained PS modified binders (PSMB) were assessed by means of a number of tests. It was observed that PS could have a different effect on binder rheology depending on its type and dosage. However, the addition of PS to base bitumen did not cause any significant variation in the rheological characteristics or PG [17]. Future production of PSMBs could significantly reduce costs for sludge management and transportation. Furthermore, relevant savings could be obtained in terms of reducing neat bitumen utilization.

A subsequent study published in 2021 demonstrated that the annual production of PS from Italian automotive factories, in the order of 3000 t/year, could be accommodated in a paved area of 1.64 km^2. Such an area corresponds to approx. 330 km if local roads, with an average width of 5 m, are considered. [43]. The cost for treating PS to be prepared for recycling was estimated at 144 €/t of raw PS, which was of the same order, or even inferior, to that required for PS incineration or disposal in a landfill for hazardous waste (250–300 €) [43]. The results of the LCA analysis revealed that the production of HMAs by employing a binder that contains 20% b.w. of PS reduced the gross energy requirement and global warming potential indexes by 15% and 39%, respectively, compared to an HMA produced with the traditional process. The two operations of producing HMAs with a PSMB and constructing the pavement were found to have a very limited environmental impact. In fact, an adequate tuning of the operating conditions of the recycling process (i.e., a drying process of PS carried out at a temperature value ranging from 105 to 150 °C) made the quality of the gaseous emissions generated from HMA production and lying very similar to that obtained by producing and lying traditional, unmodified HMAs containing neat bitumen [44]. Similarly, the presence of PS in the binder of an HMA did not negatively affect the quality of the leachate, obtained according to EN 12457/2 standard (solid-liquid ratio: 1:10; contact time: 24 h; deionized water; particle size <4 mm), in order to simulate the elution of pollutants due to runoff water on the pavement.

6. Recovery through Pyrolysis and Other Thermal Processes

Several recovery processes presented from the early 1990s to recent times are based on pyrolysis. The aim of pyrolysis is to convert PS into reusable materials in three forms, namely gaseous and liquid decomposition products and solid residues.

The two patents from Agarwal (US Patents 5,129,995 and 5,198,018) [45,46], filed in 1992–1993 were mainly intended to use pyrolysis in order to obtain a residue rich in inorganic oxides that could be reused as a paint filler. The organic components, namely pyro-oil and pyro-gas, were expected to be merely burned. According to the Agarwal's patents, an amount of approx. 25% of the dried PS could be recovered in the form of inorganic oxide material [45,46].

Some years later, researchers from the Ford company [47] investigated the technical feasibility of using pyrolysis to convert PS into:

(i) Fuels to be burned.
(ii) Activated char to be further used to capture VOCs from the exhaust air generated in painting operations.

(iii) Inorganic oxides to be recycled into new paints.

The process developed by Narula and coauthors, described in US Patent 5,543,367 [47], included a preliminary step of drying and a subsequent step of pyrolysis to be carried out in two or three stages. According to the inventors, the drying process must be carried out at a temperature below 200 °C, preferably under vacuum, for the time necessary to remove water and low-boiling organic solvents. The first stage of pyrolysis had to be carried out at a temperature below 600 °C in an inert atmosphere of either nitrogen or argon. Pyrolysis generated three products, namely gaseous and liquid decomposition materials and solid residues, which were recovered according to a ratio of approx. 1:1:1 b.w.

The gaseous product could be trapped and cooled in an isopropanol bath so as to convert it into a liquid form for easier handling. Chemical analyses revealed that the main substances found in the gaseous fraction were hydrocarbons or organic compounds like 2-butene, 1-methoxy-1-propene, or their isomers. They can be used as precursors for the preparation of carbon and fuel gases, as shown in Figure 6.

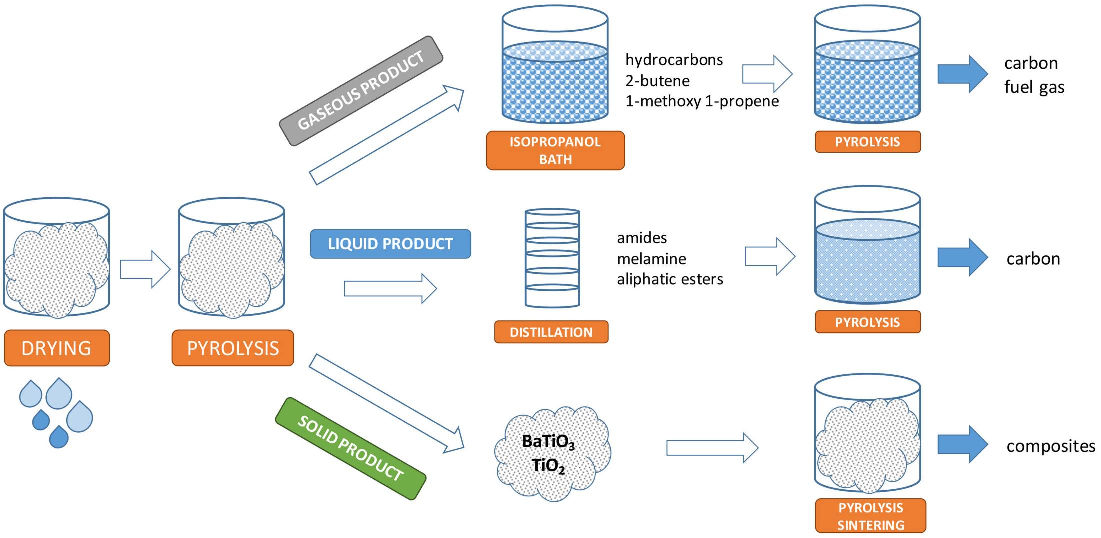

Figure 6. Scheme of the recycling process [47] aimed at producing carbon, fuel gas, and composites through pyrolysis of PS.

The collected liquid was found to contain a variety of organic polymers, which included amides, melamine, and aliphatic esters but no aromatic compounds. A distillation process can separate the liquid product into various fractions [47]. The collected gaseous and liquid decomposition materials can undergo a further pyrolysis process carried out at temperatures in the range between 800 and 1200 °C in an inert atmosphere of either nitrogen or argon. Gaseous and liquid decomposition products can be collected (separately or together) and maintained at that elevated temperature for a time sufficient to convert gases and liquids to carbon products. Various shapes and forms (amorphous or turbostratic) of carbon materials may be prepared, depending on the pyrolysis conditions. Carbon products may be used in numerous applications, namely as carbon black fillers, carbon-carbon composites, and carbon-ceramic composites.

Finally, the solid residue, with particles in the range of 0.2–0.3 µm, was found to contain barium titanate ($BaTiO_3$) and rutile titanate dioxide (TiO_2), which are of interest for the production of composite materials. The sintering of the composites required a further step of pyrolysis, carried out at an elevated temperature (900–1300 °C) in an inert atmosphere obtained with nitrogen, argon, or ammonia. The specific composition of the composites in terms of titanium compounds depended on the pyrolysis conditions. The composites were incorporated into other materials to act as reinforcing fillers [48].

In another study, the same group of authors tested pyrolysis to prepare activated carbon to be used to remove VOCs from the spray booth air [49,50]. The activated carbon obtained from a pyrolysis process carried out at 600 °C in a nitrogen atmosphere with KOH as an activating agent was a high-surface-area char containing inorganic oxides. According to the inventors, that process could recover approx. 30–40% of the initial mass of the dried PS. They observed that the adsorption capacity of the activated carbon obtained from PS was only 5–20% that of widely used commercial activated carbons and depended on the characteristics of the starting PS. In fact, chars from black paint had substantially larger surface areas and adsorption capacities, whereas chars from white paint had a higher ash content. That was due to the fact that carbon black, which is the substance used as black pigment, is the basic ingredient of activated carbon; conversely, titanium dioxide, which is the white pigment, contributed to the large ash content. The adsorption capacity of the activated carbon obtained from PS could be improved by adding supplementary carbonaceous materials.

In this regard, Li et al. [51] recently demonstrated that PS can act as a pore-forming agent in the preparation of SS-derived carbon (SC). SCs are of interest for use as catalyst supports. The PS used in that study showed a weight loss of 98.5% at 600 °C, thus suggesting that it originated from clearcoat deposition. The almost complete weight loss of PS, either by itself or in combination with another substrate, such as SS, demonstrated its potential to be a pore-forming agent in a carbonization process. Carbonization was obtained in a tube electric furnace at a rate of 10 °C/min to 600 °C and subsequently held for two hours in the presence of nitrogen gas. The products of decomposition, namely water, carbon dioxide, and other volatile hydrocarbons, generated pores, therefore decreasing the bulk densities and increasing the S_{BET} (specific surface area measured by nitrogen adsorption-desorption, 7.7 m^2/g vs. 84.2 m^2/g). However, excessive volatiles and gases could increase the number of pores and make the pore wall pretty thin. That finally caused the collapse of the pores with an increase in bulk density and a decrease in S_{BET}. The study demonstrated that PS was very efficient for fabricating macropores but had a very limited capacity for generating micro- and mesopores, which could be obtained with the addition of $ZnCl_2$ (S_{BET} = 680.5 m^2/g) [51].

Idris et al. [52] proposed a two-stage microwave pyrolysis to produce activated carbon to be used as a supercapacitor. A first pyrolysis process (1000 W, 30 min) transformed raw PS into a char material with a hard structure. The char was crushed to a size of around 1 mm, and larger particles were removed by sieving. The char was mixed with a 5M KOH solution (1:3 b.w.), impregnated overnight, and then carbonized in a microwave oven under various operating conditions (600, 700, and 1000 W for 10, 15, and 30 min) in the presence of a protective atmosphere of nitrogen. The study demonstrated that the combination of high powers and contact times (1000 W, 30 min) produced activated carbon with a S_{BET} of 152 m^2/g and a total pore volume of 0.157 cm^3/g. Better results were obtained when the contact time was increased to 45 min, but in this case the value of S_{BET}, 434 m^2/g, was too low to make the activated carbon suitable to be used as a supercapacitor ($S_{BET} > 1000$ m^2/g) [52].

Muniz et al. carried out tests of pyrolysis on three samples of PS containing different types of resins, namely alkyd, latex, and polyurethane [53]. Tests were carried out at temperatures ranging from 450 to 650 °C for 10–90 min. The tests were aimed first at extracting liquid and gaseous products with a high heat of combustion and, second, making PS chemically inert. The authors obtained liquid product yields of 34%, 56%, and 63% for alkyd, latex, and polyurethane resin, respectively. The observed average reduction in the weight of the initial solid mass was 70%, 75%, and 96% for alkyd, latex, and polyurethane, respectively. Eventual gas products were not quantified. At the end of their study, the authors mentioned an economic analysis that should have been carried out in order to quantify operational costs and revenues from liquid and gas products, but, to the best of our knowledge, the results of such an analysis were never published.

Rosli et al. carried out a pyrolysis process on a sample of PS collected at an automotive manufacturing industry located in Malaysia [54]. The pyrolysis was carried out using a microwave (600 W, gas sampling times of 20, 30, and 40 min) in order to obtain pyro-gas, which was analyzed with a GC-FID. The obtained chromatogram showed the existence of at least one organic compound detected with the FID, but the observed peak had a retention time that was slightly higher (approx. 3.28 min) than that of pure methane (2.85 min). Further analyses are deemed necessary to better characterize the gas product obtained from pyrolysis.

The studies reported in this section demonstrated that pyrolysis could be a promising process for the recycling of PS. Pyrolysis can extract liquid and gaseous fuels and produce organic and inorganic solid materials, which are of interest for the painting operation. However, to the best of our knowledge, the experiences reviewed in this paper were carried out only at a small (lab or pilot) scale and were not supplemented with a cost analysis. Consequently, it was not proven that pyrolysis could be a competitive solution for the recovery of PS.

7. Recovery and Treatment of PS through Biological Processes

A number of studies carried out in the last 10 years tested the capacity of aerobic biological processes to reduce the hazardous potential of PS and eventually produce some benefits for the environment.

The works of Tian et al. [14,36,55] focused on the fate of melamine resin (MR) in composting and the subsequent effects of compost application on plant growth and soil water quality. Melamine, a compound belonging to the family of triazine, is used in several industrial products, often in combination with formaldehyde to produce MR. Melamine formaldehyde resins have hard and durable properties, which make them suitable for use in the formulation of automobile paints. Consequently, MR is found in PS. Melamine at concentrations higher than 1 mg/L was found to have an inhibitory capacity in the biological processes specialized in nitrogen and phosphorous removal from wastewater. Otherwise, it seems to promote the activity of glycogen-accumulating organisms (GAOs), that is, the organisms that compete with the phosphorous-accumulating organisms (PAOs) in taking up readily biodegradable compounds in anaerobic-oxic (A/O) wastewater treatment schemes [56]. In the studies of Tian et al. [36,55], the MR content of the two samples of basecoat and clearcoat PS was in the order of 0.8–1.0 g/kg dry matter. Because of the high nitrogen content of MR and its potential inhibitory capacity, PS was mixed with other waste products, namely waste paper and plant residues, as a nitrogen source in the composting process. The mixture with waste paper was found to be the most promising substrate, with a reduction of the MR content of more than 80% after 84 days. Furthermore, the compost obtained from PS and waste paper increased the biomass of cucumber, radish, and lettuce compared to the control. The concentrations of metals in the harvested plant biomass and in the soil water did not rise to a level that would preclude the so-obtained compost from being used as a soil amendment [36,55].

The promising results found in the two previous studies [36,55] encouraged the authors to validate the process at a larger scale by using a commercial-scale windrow process. In that new study, the authors evaluated how the C/N ratio affected the degradation of MR and its derivatives [14]. They found that low C/N ratios, obtained by mixing PS with oat and hay straws, promoted MR degradation. In fact, after 98 days of composting, they observed the highest efficiency in MR degradation (87.5%) at the C/N ratio of 30 and lower values at higher C/N ratios (from 33 to 37). They also found significant amounts of plant nutrients in the final composts, while heavy metal contents were well below the values considered to be of concern for surface water quality or crop production [14].

Salihoglu et al. investigated the compostability of water-based PS [15]. They used the sludge separated by flotation from the wastewater generated in painting operations as additional substrate and corncob as a bulking agent in order to provide optimum porosity to the composting substrate. The amount of PS was from 55% to 85% of the overall mass of the composting substrate. An increase in temperature sufficient to reach values of more than 40 °C for at least 5 days was observed for all mixtures made of PS, wastewater sludge, and corncob. The occurrence of the composting process was verified through the increase in the composting temperature, which is an indication of the promotion of the native microbial population and its activity. Losses in the content of organic matter, between 4.2% and 17.1%, a decrease in the C/N ratio, between 5.5% and 35.4%, and, finally, a BTEX reduction in the order of 70% were observed in the tested systems. However, nickel and tin levels in the final product exceeded the limits fixed by Turkish law for the agricultural use of compost products. The heating value of the compost mixtures doubled (passing from approx. 9500 to 18,800 kJ/kg) from the beginning to the end of the composting process. That evidence allowed for composting to be considered a feasible option to bio-dry PS before using it to integrate conventional fuels in cement factories, foundries, or other thermal plants [15].

Additionally to the traditional processes of composting, vermicomposting supported by *Eisenia fetida* earthworms was tested in order to reduce the hazardousness of PS, specifically for what concerns the content of chromium [57] and BTEX [58]. In the case of chromium removal, because of the presence of BTEX, heavy metals, and other toxic compounds in the PS collected at the Iranian Automobile Manufacturing Company (Saipa), the composting process was carried out on a mixture of PS and SS under different proportions (from 1:16 to 1:1). Reduction of the Cr^{6+} concentration from 5 mg/kg to 0.2 mg/kg was observed after 60 days in the 1:10 mixture. In the second study, the original concentration of BTEX in PS was in the order of 250 mg/kg. PS was mixed with biological sludge in proportions ranging from 1:0 (for PS only) to 1:16. The authors observed that only ratios inferior to 1:10 determined significant worms' proliferation and reduction of organic pollutants. At higher PS/biological sludge ratios, the vermicomposting process seemed to be inhibited. The observed reduction in the BTEX concentration could be due to a synergistic effect between biological degradation and the high volatilization potential of the considered substances [58]. Conversely, the reduction in the chromium concentration in [57] could result from the dilution operated by another substrate on PS.

Recently, bioleaching processes have been tested in order to reduce the heavy metal content of PS [59,60]. Bioleaching can transform solid compounds into extractable and soluble elements using bacteria and fungi [61,62]. *Acidithiobacillus thiooxidans* was one of the most extensively studied acidophilic and chemoautotrophic bacteria in bioleaching processes involving SS, contaminated sediments, and mine tailings [63]. *A. thiooxidans* can obtain energy and electrons from the oxidation of reducible sulfur, which is oxidized to sulfuric acid and used to extract metals. *A. thiooxidans* was deemed very promising for this aim because it has a high acid resistance and a high tolerance to metal ions such as copper and zinc. Honarjooy Barkusaraey et al. cultured *A. thiooxidans* in a specific medium and, subsequently, adapted the culture to PS through subsequent adaptation steps [59]. The removal of zinc from PS in the order of 20% was obtained in PS slurries of 10 g/L at acidic pH values (4.2). The same authors, in a subsequent study, isolated *Pseudomonas aeruginosa* from water-based PS [60]. *P. aeruginosa* is an indigenous, heterotrophic microorganism that uses a source of organic carbon to grow and produce organic acids that act as leaching agents under appropriate conditions. Under the optimal operating conditions (pH = 7, T = 32 °C, particle size of 3 mm), *P. aeruginosa* proved to be capable of reducing the zinc content in PS by approx. 27%, probably through a mechanism of adsorption.

In the latest years, the substitution of organic solvents with eco-friendlier water-based systems made paints (and, consequently, PS) more susceptible to biodegradation processes. The development of bacteria, molds, and yeast in water-based paints is a frequent cause of paint deterioration unless biocides and preservatives are added [64], but can be beneficial for the biological detoxification of PS. Recently, Honarjooy Barkusaraey et al. isolated and identified six colonies of resistant microorganisms in a culture of automobile PS [65]. The main microbial consortiums isolated from PS included *Pseudomonas aeruginosa*, *Staphylococcus haemolyticus*, *Micrococcus yunnanensis*, *Rothia amarae*, *Gordonia terrae*, and *Brevibacillus agri*, 83% of which were gram-positive. Microorganisms were isolated using serial dilutions, direct cultivation, and enrichment methods in basic salt cultivation media. The presence of microorganisms resistant to inhibiting compounds, such as heavy metals and biocides found in PS, made the bio-attenuation of the hazardousness of PS with indigenous microorganisms an option that deserves to be further investigated.

8. Other Processes

Attempts were made to use PS as a substitute for bentonite clay in the production of iron ore pellets for the iron- and steelmaking industries [66]. Bentonite clay is the typical binder used for the production of iron ore pellets, but its high costs suggest looking for a cheaper alternative. Furthermore, the typical mineralogical composition of bentonite clay provides the iron ore pellets with an increase in the alumina and silica content. That is deemed detrimental in the ironmaking process because it determines an increase in the slag acidity with a consequent increase in slag viscosity, which makes the slag tapping a more difficult process. A number of 38 mixtures of magnetite ore (96–100%), limestone (0–3%), bentonite (0–1%), and PS (0–1%) were prepared according to a half-factory design and then subjected to an induration process at temperatures from 870 to 1150 °C for 30–90 min. The so-obtained iron ore pellets were tested for green crushing strength (ASTM E382-20), cold crushing strength, drop test, apparent porosity (ASTM C20-00 (2015)), and percent reduction, properties that were deemed to be important for the durability and efficiency of the iron ore pellets. The authors found that the iron pellets where bentonite was partially or completely replaced with PS had cold crushing strengths values greater than the threshold of 250 kg/pellet fixed by industrial standards, provided that the induration process was carried out at the highest temperature value (1150 °C). Furthermore, the values of drop, apparent porosity, and percent reduction were in line with the standards, thus making PS a promising substitute for bentonite in the production of iron ore pellets.

Some studies were not aimed at recovering PS but only at reducing its hazardousness for landfill disposal. Arce et al. [67] tested a solidification/stabilization (S/S) process as an immobilization pre-treatment of an alkyd solvent-based PS, coming from the automotive industry, prior to the disposal in a landfill [67]. The S/S process was based on accelerated carbonation obtained with different substances, namely lime, lime-coal, fly-ash, and lime-Portland cement. The effect of the water/solid ratio and carbonation time on the characteristics of the final product was studied. Metals, anions, and dissolved organic carbon (DOC) were analyzed in the leachates obtained from a series of compliance and characterization leaching tests aimed at assessing the efficiency of the treatment in immobilizing contaminants. The lowest DOC concentrations in the leachates (400 mg/kg DOC in L/S = 10 batch leaching tests) were obtained when carbonation of PS-lime-fly-ash mixtures was carried out for 10 h at a water-to-solids ratio of 0.2. The flammability characteristics, the total content of contaminants, and the contaminant release rate in compliance leaching tests provided evidence for a final product suitable to be disposed of in non-hazardous landfills. A similar approach was followed also by Hoang and Vu [68], with the aim of producing an inert material to be used for construction or as a reinforcing material. In their study, they test the feasibility of making PS inert through a two-step solidification process. PS were sun-dried to a final TS content of 60–70%, then they were first mixed with cement, sand, and a calcium carbonate ($CaCO_3$) solution. In the second step, the resulting mixture was mixed with ultra-fine fly ash and silica fume in order to fill the pores and increase the efficiency of solidification. The mixtures contained 60–70% PS and 30–40% additives. Mixtures were tested according to the EPA Toxicity Characteristic Leaching Procedure (TCLP) in order to evaluate the efficiency of the process in reducing the release of chromium, cadmium, and lead. Hoang and Vu demonstrated that appropriate ratios among PS and the above-mentioned additives could make the mixture compliant with the Vietnamese standard for heavy metals [68]. In the conclusions, the authors mentioned a procedure of cost analysis used to evaluate the treatment costs. However, no details of it were provided; the authors only claimed that the tested solidification process was competitive compared to other treatment solutions, such as inertization with surfactants, incineration, or landfilling.

Gautam et al. presented the results of a trial that involved the co-burning of PS in a cement kiln [9]. The PS generated in the Toyota Kirloskar Motors Limited plant in Bangalore, India, was firstly dewatered with the aid of a wire sieve placed on a rectangular collecting tank, and then the separated solid part of the waste was packed into bags weighing approx. 5.5 kg each. After a period of stabilization (the pre-co-processing phase), during which the kiln was fed with the conventional fuel (coal), bags of PS were fed for approx. 8 days. For the whole duration of the trial, the operating parameters of the process were monitored and the flue gases were sampled and analyzed. The co-burning process was carried out at a temperature of 1400–1450 °C for 4–5 s. The comparison of the quality of the flue gases between the co-processing phase and the pre-co-processing phase revealed a decrease in the emission of dioxins and furans (−8%), TOC (−20%), CO (−30%) and heavy metals (−57%), a slightly increased emission of particulate matter (+13%), and a substantial increase for NOx (+80%). The concentrations registered for particulate matter and NOx were in any case below the values fixed by the norms for the common hazardous waste incinerators. No evident changes were observed for the other parameters of interest (HCl, HF, SO_2, and Hg). Although co-burning at cement kilns is a common management route worldwide, only a limited number of studies have reported the influence of this option on emission characteristics. As the air pollution control units of cement plants were designed to control particulate matter resulting from the combustion of non-hazardous raw materials, not the gaseous and particulate matter resulting from hazardous waste materials such as PS, this field requires more research to see the changes in the emissions as the amount of PS to be burned is increased.

The thermal valorization of PS through its transformation into a combustible fuel product is the topic of US Patent 8,057,556 B2 by McCarty et al. [3]. The process described there included a preliminary phase of dewatering, during which the PS was concentrated to approx. 50% TS, and a subsequent phase where the resulting PS was mixed with a carbonaceous material to produce a combustible fuel. The focus of the invention was the dewatering operation, which, according to the inventors, could be carried out by filtration, filter pressing, centrifugation, decantation, distillation, extraction, freeze drying, fluidized bed drying, and similar processes capable of removing excess water. The patent suggested using a dedicated decanting hopper, with a very limited need for electrical energy, through two or three decanting stages. The transfer of the PS from one hopper to another resulted in an agitation that chummed and mixed the PS, thus determining an improved and more homogenous consistency, which promoted further releases of water in the subsequent decanting stage.

Finally, Lappänen et al. presented a descriptive case study concerning the feasibility of recycling PS in the context of Northern Ostrobothnia, a region of Finland [69]. In that study, aqueous PS generated in painting processes carried out at sawmills and window and door frame manufacturers was sampled and characterized through an XRF analysis. The analysis revealed that carbon, titanium, aluminum, and silicon were the most abundant elements, with amounts of approx. 32%, 17% (as TiO_2), 17% (as Al_2O_3), and 7% (as SiO_2), respectively. The options for PS valorization considered in the study, only from the point of view of a literature analysis, were (i) the extraction of valuable components, such as barium, titanium dioxide, or aluminum; (ii) the utilization as a chemical catalyst because of the presence of aluminum, titanium, and silicon; (iii) as a raw material for the production of new paints; and, finally; (iv) as a substitute fuel in cement kilns [69]. The authors concluded that the solutions involving the extraction and re-use of some compounds (i–iii) must be better assessed in terms of their technical feasibility. They identified a further challenge related to PS utilization, namely the logistics for narrow material flows coming from decentralized sources in a relatively large geographical area. In fact, often, circular economy solutions are formed around major industrial companies where the volume of generated side streams allows for economies of scale.

9. Conclusions

Finding solutions for the PS which is yearly produced in the automotive industry in the order of 200,000–500,000 t, is an urgent issue. Such waste is usually disposed of in landfills, after chemical or biological stabilization processes, or incinerated. However, in order to comply with the principles of the circular economy and limit the construction of new landfill sites, other solutions are necessary.

Because of the high organic content of the PS that comes from solvent-based paints, processes for their utilization in the production of primers and sealants have been patented. However, those processes include several operations and require reagents and solvents that are specific to each typology of PS. The utilization of PS for the production of building materials, namely cement concrete, mortars, or bituminous binders, seems like a more feasible option. Specifically, PS can substitute up to 20% of the neat bitumen in the HMAs used for paving applications, with a consequent saving of energy, greenhouse gas emissions, and costs for PS disposal and bitumen supply. This solution was tested at the field scale, and the positive outcomes returned by economic and environmental assessments made it ready to be applied. Conversely, the utilization of PS in concrete in amounts higher than 5% of cement replacement may result in a significant decrease in the compressive strength and should be applied with caution. This application generally requires the drying and grinding of PS before use, which necessitates additional energy use. This aspect, along with the very limited percentages of replacements, should be taken into account if the utilization of PS for cement, concrete, or composites production is considered a waste management solution.

Another promising option seems to be the utilization of thermo-chemical processes, namely pyrolysis and gasification, to convert PS into reusable materials in the forms of gaseous and liquid fuels and solid residues. Depending on the nature of the solid residues, they can be recycled as activated char, which can be further used to capture VOCs from the exhaust air generated in painting operations, or as inorganic oxides, which can be recycled into new paints. However, at present, thermo-chemical processes have been studied only at a lab or pilot scale, and there is a lack of information concerning their economic and environmental sustainability.

Another group of processes examined in this paper were biological processes. Mixing PS with biodegradable substrates allowed PS stabilization through composting. However, it has to be considered that the reduction in the contaminants (heavy metals, BTEX) concentration observed at the end of the process mainly depends on dilution, due to the mixing of PS with other substrates or volatilization. Bioleaching supported by native or exogenous microorganisms is a rapidly growing field of research that deserves further investigation to verify if it can be a feasible option to recover metals from PS.

However, most of the above-mentioned solutions require PS with a limited or no content of water. For that, processes and machines have been developed in order to, firstly, efficiently dewater the sludge and, subsequently, dry and reduce it in the form of powder or pellets to make it ready for the operations of valorization and recycling.

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