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Recycling of Waste Toner in the Republic of Croatia – An Environmentally Friendly Approach

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Large amounts of waste toner cartridges have been generated as a consequence of their use in printers and duplicators on an everyday basis. Waste toner cartridges contain heavy metals, plastics, as well as toxic residual toner powder, and have been characterized as hazardous waste. Therefore the management of waste toner cartridge content presents a significant issue in environmental protection. The use of hazardous substances in electrical and electronic equipment, as well as promoting the collection, recycling and recovery targets for all types of electrical goods was prescribed by EU legislation, particularly the WEEE Directive and, together with the RoHS Directive, has been in force since February 2003. In order to concur with the WEEE Directive, a system for the management of electrical and electronic waste has been established in the Republic of Croatia five years ago, but there was no practical possibility for the treatment of collected waste toner cartridges. In this work, a study of the possibility of waste toner cartridges and further recycling and reuse has been performed, with special emphasis on the reuse of the residual toner powder. In order to decrease explosive properties of the residual toner powder, the material was mixed with calcite. After performed analyses of the mixture it was found that the mixture cannot be disposed of on landfill sites as inert waste material, since the value of the total organic carbon content (TOC) has found to be above the limit prescribed by the law. All other analyzed parameters have found to be below the limits prescribed by the law. Moreover, it was found that the mixture of residual toner powder, which contains 10 % of calcite, is an excellent bitumen additive, since it improves its application properties. So, the mixture of the residual toner powder and calcite can be used as a valuable raw material in the production of bituminous products and in different construction works.

1. Introduction

Every year, a tremendous amount of toner is produced and used worldwide in copiers and printers. Spent toner is the residue left in cartridges in copiers and printers (Hansen et al., 2000). EU legislation prescribes the use of hazardous substances in electrical and electronic equipment as well as encouragement of collection, recycling and recovery issues of all types of electrical items by the means of the WEEE and RoHS Directives. The Republic of Croatia will soon be a full EU member and the process of adoption of EU legislation has been mostly completed. Particularly the management of electrical and electronic equipment according to the WEEE Directive has been in practice for the last five years. Approximately 10 % of toner powder remains in photocopiers, of which 66 % available for recovery is currently being recovered. Residual toner powder is of different particle size compared to the original toner, and is contaminated with dust absorbed from paper. Moreover, residual toner powder in waste toner cartridges contains several components and some of them have found to be of high toxicity for humans if inhaled, due to their small size (Salhofer and Tesar, 2011). These compounds include carbon black (polyacrylate-styrene copolymer), resins (polyethylene/polypropylene parafin wax) and charge control agents (hydroxyl-aromatic acid and derivatives) (Ruan et al., 2011). Furthermore, many tin pot toners contain polycyclic aromatic hydrocarbons and dimethyl nitrate amine (both are carcinogens) as imaging materials. Therefore,

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the recovery of residual toner powder is a vital topic, not only due to rules prescribed by the law, but also from the resource reutilization and environmental protection point of view. Since there was not any better way of utilizing the residual toner powder from copiers and printer cartridges, the material has been dumped into landfills in the past. Landfilling and incineration are not suitable for dealing with residual toner powder, as furan and dioxin gases may be produced. Disposal of residual toner powder to landfills can pollute the environment due to leakages. Incineration of residual toner powder, on the other hand, is not a refined treatment solution due to macromolecular organic compounds composition. Moreover, due to small particle size, airborne toner may present an explosion hazard. Waste toner cartridges, beside toner powder, contain valuable material, such as aluminium and plastic (Ruan and Xu, 2011). The usage of residual toner has already been described in literature by Yildirim et al. (2004) and Ruan and Xu (2011).

Bitumen is a thermoplastic liquid and at high temperature or low loading it behaves as a viscous liquid. This classical dichotomy creates the need to improve its performance as an asphalt binder to minimize the stress cracking that occurs at low temperatures and the plastic deformation (rutting) at high temperature. In order to increase the durability of bitumen, it needs to be modified (Eweed, 2011). Also, it is well known that that the polymer modified asphalt has the superior property, such as fluidity-resistant, abrasion-resistant and draining property, as binder in the pavement. The output of modified asphalt increases every year and for example, in Japan, exceeds 430.000 t (Sugano et al., 2009).

The addition of any non-bituminous component to a bituminous paving mixture causes physical and chemical changes in the properties of the original material components (Hansen et al., 2000; Kelly, 1993). Chemical compatibility of the components has the most significant influence on the quality of the resulting mixture.

Due to the increase of necessity for regular management of waste toner cartridges in the Republic of Croatia, an estimation of the annual amount of collected and reused cartridges based on data of producer/holder requests and demands have been made. It is possible to envision that the collected amount of waste toner cartridges will exceed 75 t/y. This amount includes waste cartridges which have been placed or used in the following equipment: printers, facsimiles, multifunctionals and other items.

The scope of this work was to find a recycling solution for residual toner powder originated from waste cartridges, since the powder has been recognized as hazardous waste and cannot be disposed of on sanitary landfills. Therefore, the addition of toner powder to bitumen, as well as physical properties of the obtained mixture was studied.

2. Methodology

Waste cartridges have been collected and transported to one of the locations of the company SPECTRA-MEDIA Ltd. for temporary storage and reuse. The material has been mechanically disintegrated by a device for recycling of waste toner cartridges with the capacity of 250 – 300 kg in one working shift. During the disintegration process, plastic material, metals (iron and aluminum) and residual toner powder have been detached (Figure 1). Separated plastic material has been treated in the SPECTRA-MEDIA Ltd. unit and iron and aluminum distributed to the market as valuable secondary raw materials. Residual toner powder has been separated on a console equipped with a dust vacuum device that does not allow uncontrolled emissions of the toner powder to the environment. The residual toner powder has been collected in the filter of the vacuum device and subjected to temporary storage. Since the toner powder was classified as hazardous waste it has been delivered to a certified company for further management.

During this recycling process, calcite (calcium carbonate) in the amount of 50 % was added in order to decrease the possibility of inflammation and explosion. A sample of the mixture of calcite and residual toner powder was taken out from the process of disintegration (m(sample) = 4 kg). The total moisture, ash, total incombustible compounds, combustible compounds, volatile compounds, volatile without the moisture as well as the coke residuum were determined for the sample. Additionally, the sample was analyzed in order to determine the maximal explosion pressure of the dust cloud according to EN 14034-1:2004, maximal velocity of the cloud explosion pressure (EN 14034-2:2006), and the lowest level of the dust cloud explosion. The parameters were determined at a temperature of T = 22 - 24 ºC, and relative humidity R_H = 52 – 56 %. All parameters were determined by the authorized Agency for explosive atmosphere hazardous areas, Laboratory for explosion protection ExLAB, Zagreb, Croatia. Determination of the powder explosion characteristics was performed using a sphere of a 20 L volume (Figure 2) according to the procedure described by Beck et al. (1997).

Figure 1. Device for recycling of waste toner cartridges

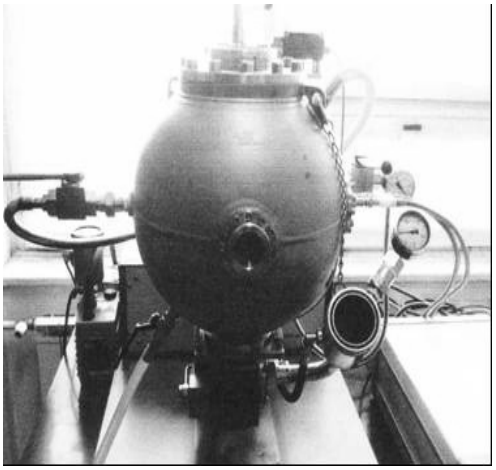

Figure 2. Investigation device for determination of powder explosion characteristics

The analysis of the physical and chemical properties of the mixture of calcite and residual toner powder was performed by the Department of Public Health, Dr. Andrija Štampar, Zagreb, Croatia, in accordance with the prerequisites of the HRN ENISO/IEC 17025 standard (2013).
On an industrial scale, the mixture of residual toner and calcite has been tested as a partial substitute for conventional fillers. About 35 % of pure calcite usually added to a single batch of joint sealant has been replaced with calcite contained in the added residual toner mixture. Due to a lack of knowledge about the exact composition of the residual toner, i.e. its polymer content, the quantity of virgin polymer filler needed to be left intact, in order to assure the product's compliance with EN 14188-1. The total amount of toner mixture added to one batch of joint sealant was 160 kg (~ 10 %).
One of the standard specification tests for bitumens and bituminous products is the determination of their softening point, which is defined as the temperature at which the tested substance, under specified conditions, attains a particular degree of softening. The softening point is useful in the classification of bitumens into different grades, and in this investigation it has been tested according to the European Standard EN 1427, that is, with the help of the Ring and Ball apparatus.

3. Results and discussion

Based on the current experience in Croatia, from an amount of 75 t of waste toner cartridges collected in one year, after addition of calcite, 11.25 t/y of the mixture of the residual toner powder and calcite have been generated. In order to decrease the possibility of an explosion of the residual toner powder, it was mixed with calcite at a ratio of 50 : 50. The mixture was subjected to analysis in order to determine the ratio of incombustible, i.e. combustible content. The results are shown in Table 1. The contents of combustible and volatile compounds, as well as coke residuum of the mixture, were found to be lower, in comparison with the virgin residual toner powder.

Table 1: Analysis of the mixture of the residual toner and calcite (50 : 50)

Total Moisture, %	Ash, %	Total incombustible compounds, %	Combustible compounds, %	Vaporizable compounds, %	Volatile without moisture, %	Volatile compounds, %	Coke residuum, %
0.05	50.27	50.32	49.68	41.26	41.21	82.95	58.74

Furthermore, the mixture was subjected to determination of explosion characteristics. Namely, the explosive limits of many materials vary from 10 g/m^3 to about 500 g/m^3. It may be assumed that 30 g/m^3 is the lower explosive limit for most flammable dusts. Though this may seem to be a very low concentration, in appearance a cloud of dust of such a concentration would resemble a very dense fog (Cashdollar, 2000). The results of the explosion characteristics of the dust cloud are shown in Table 2. It can be seen that the maximal explosion pressure of the dust cloud of concentration 750 g/m^3, as well as the maximal velocity of the pressure increase, are lower for the mixture for the toner and calcite mixture (50 : 50) than for the virgin residual toner.

Table 2: Explosion characteristics of the dust cloud, concentration 750 g/m^3

Maximal explosion pressure; p_{max}	6.8 bar
Maximal velocity of the pressure increase; $(dp/dt)_{max}$	444 bar/s
Explosion constant; K_{st}	121 m bar/s St 1
The lowest level of the dust cloud explosion, LLE	40 g/m^3 +/- 10 %

On the basis of the analysis of physical and chemical properties of the inactive mixture of calcite and residual toner it was found that leachate has not fulfilled prerequisites for disposal to landfills, according to the Ordinance about procedures and prerequisites of the waste disposal categories and conditions for the waste landfill operation (OF 117/07). Measured values have found to be below limitations determined as the maximal allowed concentrations (MAC) for all parameters, with the exception of total organic carbon (TOC) content, which exceeded the MAC almost four times. Therefore, the obtained mixture of the residual toner and calcite cannot be disposed of as part of sanitary landfill waste without additional treatment. Regarding the properties of the inactive mixture, it could be used as filler in bitumen and asphalt manufacturing for the purpose of road construction (Yildirim et al., 2004). Previous studies concerning variation of thermoplastic copolymer content in order to improve the performance of asphalt binder showed that a polymer content of 11 % give modified mixtures maximal stability (Eweed, 2011). So, in this study, 10 % of toner addition was applied and the properties of road construction bitumen have been analyzed according to Superpave specifications. Results are shown in Table 3. Based on the results, bitumen 50/70 could be classified as bitumen PG 64 -18, and bitumen 50/70 + 10 % powder toner as PG 70 – 16, although technical properties of bitumen at low temperatures (crawling strength and m-value) have not been determined.

In order to determine the softening point, the Ring and Ball method has been used. The results are shown in Table 4. It can be seen that the addition of waste toner produces minor changes in softening point, which suggests that the waste toner does contain a sufficient amount of polymer to produce such a change. It has been noted that the polymer surplus decreases elastic deformation of the produced joint sealant at lower temperatures, as well as its adhesive properties, but further tests should be performed in order to obtain more precise results.

Table 3: Results of the analysis of the road construction bitumen sample 50/70 and road construction bitumen 50/70 with addition of 10 % of the waste toner

Property	Unit	Results of analysis 50/70	Results of analysis 50/70 + 10 % of the waste toner	Quality standard HRN EN 12591 50/70	Method of analysis
Appearance	-	Homogeneous, without additives and contamination	Homogeneous, without additives and contamination	Homogeneous, without additives and contamination	HRN EN 1425
Penetration, 25 °C	1/10 mm	55	39	50 - 70	HRN EN 1426
Mollification point	°C	50.4	54.9	46 - 54	HRN EN 1427
Density, 25 °C	kg/cm^3	1008	1020	-	HRN EN 15326
Refraction point by Frass	°C	-18	-15	≤ -8	HRN EN 12593
Ignition point	°C	> 260	> 260	≥ 230	HRN EN 2592
Soluble in toluene	%	99.7	97.9	≥ 99.0	HRN EN 12592
Weight change	%	0.06	0.02	≤ 0.5	HRN EN 12607-1
Retained penetration	%	65	72	≥ 50	HRN EN 1426
Mollification point	°C	56.2	59.5	-	HRN EN 1427
Increase of the mollification point	°C	5.8	4.6	≤ 9	HRN EN 1427

Table 4: Determination of softening point – Ring and Ball method

Samples	Softening point of joint sealant, °C	
	Without addition of waste toner mixture	With addition of waste toner mixture
1a)	101.9	104.5
1b)	100.5	104.1
2a)	100.7	102.8
2b)	101.3	104.2

4. Conclusion

The purpose of this work was to investigate a novel and more eco-friendly technique of recycling waste toner cartridges, i.e. the contained residue toner powder, as its toxicity presents a threat to the environment if solely disposed of on landfills or treated by incineration. A mixture of virgin toner powder and calcite was, therefore, tested as a substitute for fillers in the production of bituminous products. Based on the comparison of acquired softening point values for samples containing the toner mixture versus genuine samples, it can be concluded that the final product benefits from the addition of residual toner powder. Consequently, costs for additional treatment of the inactive mixture and landfill disposal can be avoided and an additional economical and ecological benefit for the society generated, which is in accordance with the waste management strategy in the Republic of Croatia.

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