International Scientific Journal
Environmental Science
http://environment.scientific-journal.com

Utilisation Options for Waste Toner Powder

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Abstract— **Daily use of electrical and electronic equipment and the rapid development of modern technologies in this area lead to the generation of significant quantities of electronic waste. This group of waste includes printers, photocopiers and fax machines that use toner powder for recreating text and images. The composition and particle size turn the disposal of the quantities of waste toner into a serious problem. Main components of toner powders are styrene acrylate copolymer, iron oxide, carbon black, polymethyl methacrylate, amorphous silica, pigments, polypropylene, waxes, and various additives (e.g. titanium dioxide). Some of these ingredients are recognised by the U.S. Environmental Protection Agency as hazardous to human health and the environment, while carbon black is classified as possibly carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer. The fine toner particles (>10 μm) may remain suspended in the air for some period of time, which can cause the occurrence of certain negative health effects. The environmental risks associated with the improper disposal of waste toner powder are discussed in the publication. An analysis of the test results of four samples waste toner (black, cyan, magenta and yellow) is carried out. The tests were done by means of weight analysis, atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), infrared spectroscopy (IR spectroscopy), thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The possibility for utilisation of spent toner as a filler and colorant in the rubber manufacturing process is assessed.**

Keywords—waste; toner powder; utilisation; disposal;

I. INTRODUCTION

Each year significant amounts of toner is produced and consumed worldwide. Toner powder consists of binder resin, colorants, iron oxide, charge control agents and other additives [1]. The major component of toners is the resin (45-90%), which binds and fixes the toner onto the receiver, usually paper, thus creating a permanent image [2]. The most commonly used binder resins are polystyrene, styrene acrylate copolymers, styrene-methacrylate copolymers, polyesters, epoxy resins, acrylics and urethanes. Styrene-acrylic copolymers have been most widely used because of their low cost and the ability to control the tribo-electric charge [3]. Colorants of toner powders may be either dyes or pigments or a combination of the two. Due to their high solubility in polymer resins as a colorant for black toner carbon black or iron oxide are used. Pigments used in chromatic toner powders in most cases are subject to commercial secret. Charge control agents are added to ensure the homogeneous distribution of charge among all toner particles. Other additives such as silica and titanium dioxide improve the flow characteristics of the toner particles and help prevent the formation of agglomerates [4].

In the toner manufacturing process raw materials are mixed mechanically in advance, then the mixture is transferred into a compounding process which heats the material into a homogeneous melt. The melt is cooled to form solid granules that have a size range on the order of a few millimeters [5]. The granules undergo a grinding process, which resembles a fluidized bed, where thanks to the continuous friction the granules become fragmented into particles with size smaller than 10 μm [6]. A classification process follows, where particles that are too large are returned to the grinding process; particles that are too small, are fed back into the compounding process. Particles within the desired size range are transferred to a packaging line, where the toner is packaged and sent to the consumer.

Most of the manufacturers offer recycling programs for waste powder from toner cartridges, but 80% of them require payment by the consumer [7, 8]. This leads to improper disposal of toner cartridges and toner powder remaining in them, thus entering the mixed municipal solid waste stream.

II. RISKS TO HUMAN HEALTH AND THE ENVIRONMENT

Composition and properties of toner powders render them unsuitable for storage in landfills along with municipal waste. The fine toner particles (>10 μm) may remain suspended in the air for some period of time, which can cause the occurrence of certain negative health effects associated mostly with irritation and damage of the respiratory system. Because of the high molecular weight of the styrene acrylate copolymer, the main toner component is not readily biodegradable. Given its low water solubility, the polymer is expected to have low mobility within landfill sites and the components of the environment [9]. However, due to the diverse morphological and chemical composition of landfilled waste it is not possible to draw general conclusions about the reactions that would occur as a result of the degradation of waste powder from the toner cartridges [10, 11].

Two of the ingredients in toner, carbon black and titanium dioxide, have been classified by the International Agency for Research on Cancer (IARC) as "possibly carcinogenic to humans" (Group 2B). Carbon black is used as a colorant for a variety of paints and coatings. Its main application, about 89-91% of the total global consumption, is as a reinforcing additive to rubber – to increase the resistance of rubber to abrasion, tear, fatigue and flexing. It also improves the tensile strength and other characteristics of many elastomers (natural and synthetic) [12]. The most recent review in 2006 found that there was sufficient evidence for the carcinogenic effects in experimental animals, but evidence for the existence of such an effect in humans was inadequate. The final evaluation of the IARC states that "No significant exposure to carbon black is thought to occur during the use of products in which carbon black is bound to other materials, such as rubber, toner powder, or paint" [13].

Titanium dioxide is found in small amounts in toner mixtures (<5%). Apart from it being used as an additive to prevent the formation of agglomerates in toner powders, titanium dioxide is used as pigment for coatings, plastics and rubber. Widespread use of titanium dioxide based pigments is due to their excellent resistance to chemical attack, good thermal stability and resistance to ultraviolet degradation. Titanium dioxide is also classified as a Group 2B carcinogen, due to lack of credible evidence of carcinogenicity to humans [14].

Amorphous silica is used in many applications in addition to its main use in the rubber industry, including cosmetics, paper and many other applications related to nutrition and health. It is subject to a number of toxicological studies that conclude that the effects of amorphous silica are transient and they resolute with cessation of exposure [15].

The analysis of the toner powder components considered shows that they not only do not pose a risk to the components of the environment and human health, but also have some valuable characteristics. This is a prerequisite to find a sustainable solution for the utilisation of waste toner powder in various industries.

III. EXPERIMENTAL

By means of reflectance spectroscopy were obtained spectra, consisting of reflectance areas and narrower absorption areas. Their specific form, depth and wave position are indicators for the chemical bonds in the studied compounds. Figures 1-4 show the infrared spectra of monochromatic and chromatic (cyan, magenta and yellow) waste toner powder samples.

The resulting spectra show that toner powders are a complex mixture of chemical compounds. Monotonous vibrations registered after 3100 cm^{-1} for the black toner confirm the presence of carbon black. The bands in the 2800-3100 cm^{-1} range for all samples are indicative of the aromatic ring in the molecules of the styrene acrylate copolymer. The bands in the 1400-1600 cm^{-1} range are representative for the skeletal vibration of the aromatic ring. The C-H vibrations absorbing in the 670-900 cm^{-1} range are one of the most intense in the spectra and are used to determine the type of substitution of the aromatic system.

In order to determine the inorganic components in toner powder four samples (monochromatic and chromatic) were calcinated under laboratory conditions at 850°C. To identify the elemental composition of the four samples atomic absorption spectroscopy (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) were used. The test results are presented in Table I.

TABLE I. ELEMENTAL COMPOSITION OF WASTE TONER POWDERS

Elements / Toner Type	Value, (%)			
	Black	***Cyan***	***Magenta***	***Yellow***
Si	7.05	32.2	40.83	41.05
Al	0.12	0.73	1.52	0.75
Ti	0.8	0.95	5.39	1.45
Ba	0.03	1.64	0.001	0.04
Ca	0.47	0.33	0.42	0.82
Mg	0.04	0.31	0.23	0.18
Na	0.2	0.5	0.1	0.6
K	0.1	0.55	0.3	1.65
Fe	57.86	0.35	1.1	0.35
Cu	0.22	12.66	0.1	0.62
Zn	0.68	2.65	0.2	0.95
Cr	0.04	< 0.001	< 0.001	< 0.001
Ni	< 0.001	< 0.001	0.19	0.11
Mn	0.03	< 0.001	< 0.001	< 0.001
Co	< 0.001	< 0.001	0.02	0.01
Pb	< 0.001	0.03	< 0.001	<0.001

It is apparent from the results that all toner powders have high silicon content, its highest in the yellow and magenta toners. Besides silicon, relatively high levels of iron were found in black toner (approximately 58%), copper in cyan toner (12.66%), titanium in magenta toner (5.39%) and potassium and titanium in yellow toners - 1.65 and 1.45% respectively.

For determining the energy characteristics of four waste toner powder samples the methods of thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were used. Thermogravimetric analysis (TGA) measured the mass of the samples as a function of temperature while the substance was subjected to a controlled temperature programme. Differential scanning calorimetry (DSC) measured the difference in energy inputs into a substance and a reference material as a function of temperature whilst the toner powder and reference material were subjected to a controlled temperature programme. DSC determined the enthalpy ΔH resulting from the thermal treatment and the change of heat capacity ΔC_p. Simultaneous determination through TGA-DTA/DSC measured the heat flux and the change in mass as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these characteristics not only improved the efficiency, but also facilitated the interpretation of results. Figures 5-12 show the TG, DTA and DSC curves for the samples.

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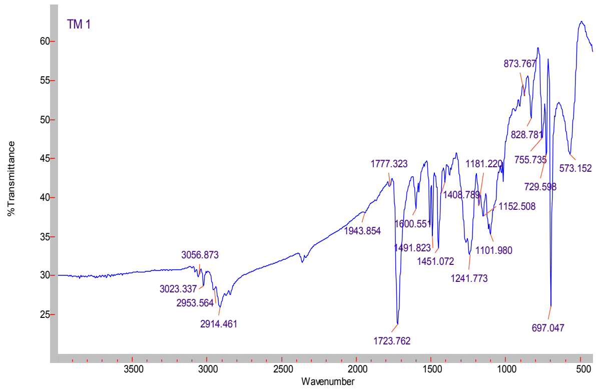

Fig. 1 Infrared spectrum of toner powder - black

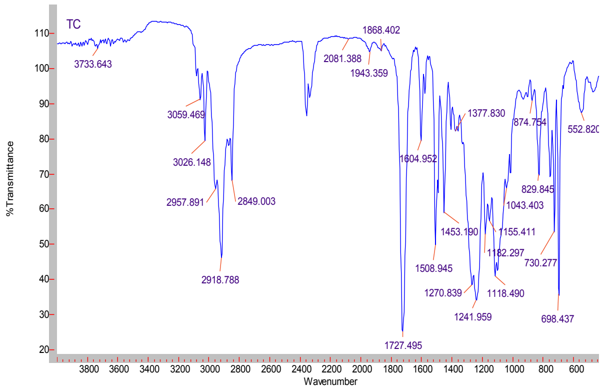

Fig. 2 Infrared spectrum of toner powder - cyan

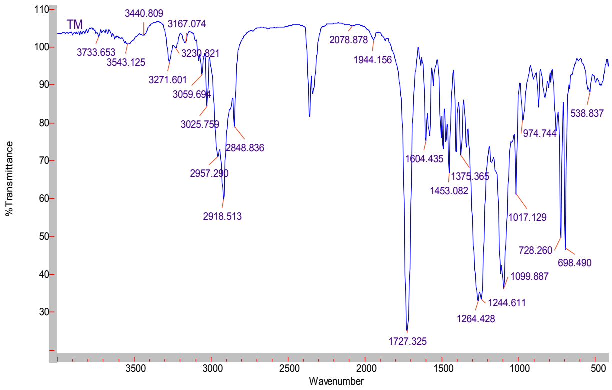

Fig. 3 Infrared spectrum of toner powder - magenta

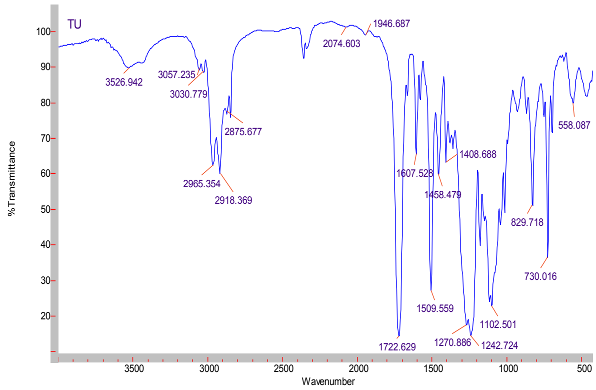

Fig. 4 Infrared spectrum of toner powder – yellow

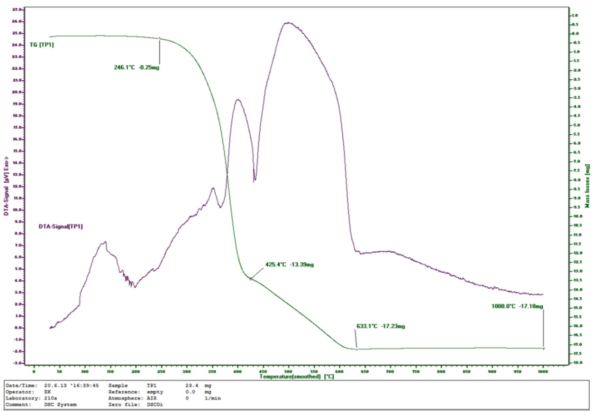
Fig. 5 TG and DTA curves for toner powder - black

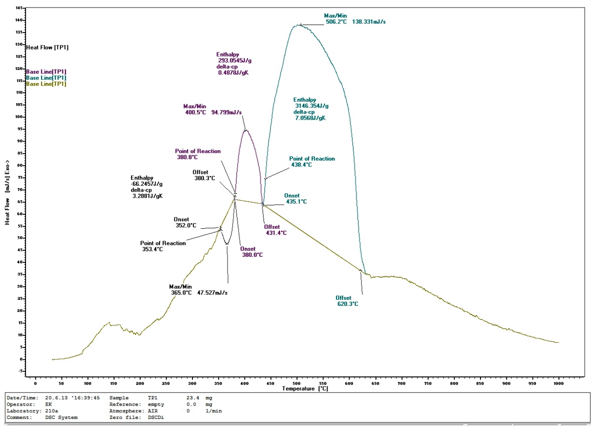
Fig. 6 DSC thermogram for toner powder - black

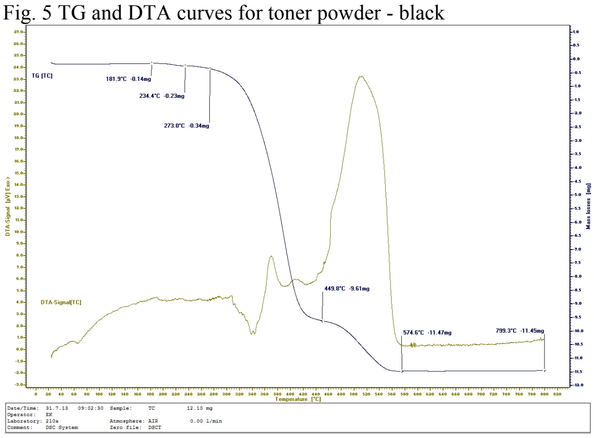
Fig. 7 TG and DTA curves for toner powder - cyan

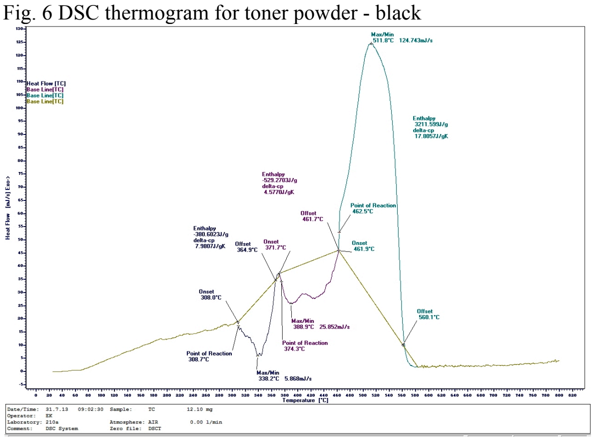
Fig. 8. DSC thermogram for toner powder - cyan

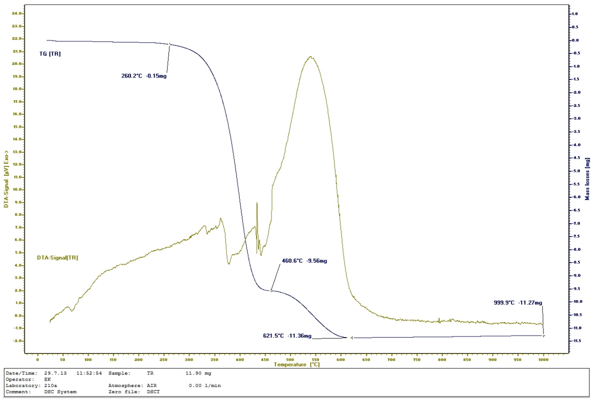

Fig. 9 TG and DTA curves for toner powder - magenta

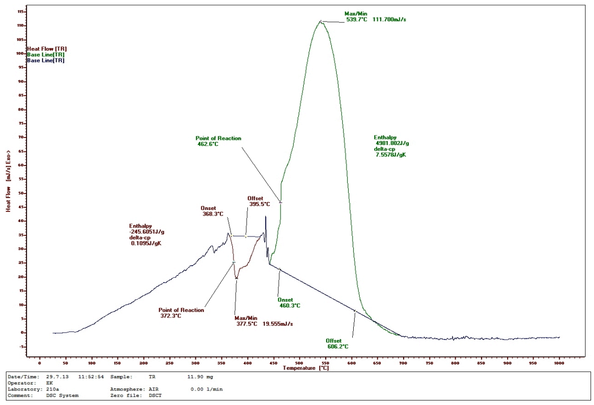

Fig. 10 DSC thermogram for toner powder - magenta

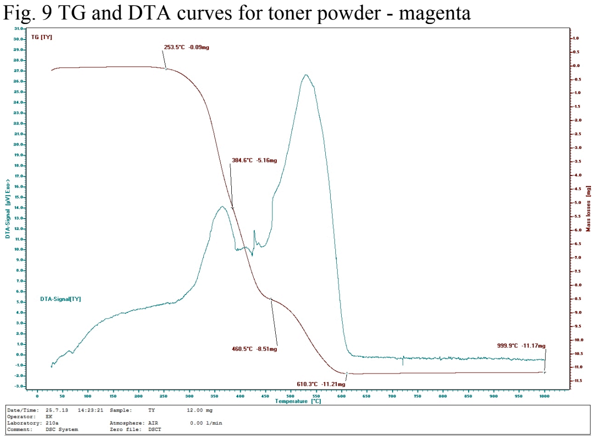

Fig. 11 TG and DTA curves for toner powder - yellow

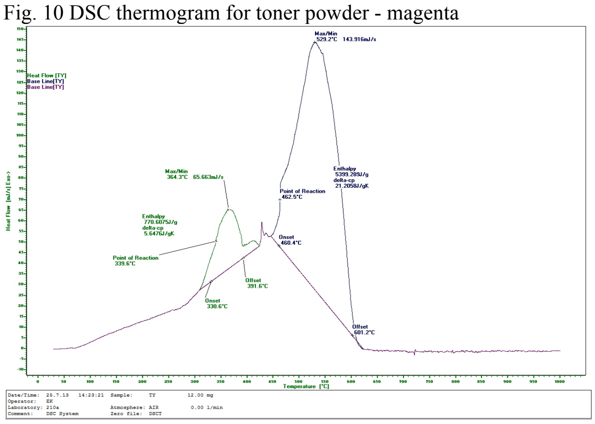

Fig. 12 DSC thermogram for toner powder - yellow

The test results are summarized in Table II.

TABLE II. COMBUSTION CHARACTERISTICS OF TONER POWDERS

Toner Type	**Initial Temperature**	**Final Temperature**	**Combustion Rate**	**Enthalpy**
Colour	***°C***	***°C***	***%***	***J/g***
Black	246.1	633.1	73.63	3373.163
Cyan	181.9	574.6	94.79	2301.726
Magenta	260.2	621.5	95.46	4736.197
Yellow	253.5	610.3	93.42	6169.897

It is evident that among the four types of waste powder from toner cartridges, yellow toner has the highest heating value - enthalpy of 6169.897 J/g, followed by magenta toner with 4736.197 J/g, which also reaches the highest combustion rate. The results show positive values for the enthalpy of all samples, which is why they are suitable for thermo-chemical treatment when the aim is energy recovery.

IV. RESULTS AND DISCUSSION

The generation of large amounts of waste powder from toner cartridges, as well as its composition requires seeking environmentally sound solutions for its disposal compliant with the European waste management hierarchy. At present the only treatment method for waste toner powder in Bulgaria is temporary storage followed by disposal through landfill, which is the most unacceptable alternative according to European legislation.

The results of the DSC analysis show that combustion of toners is accompanied by high exothermal effects. This is a prerequisite for their utilisation for energy recovery in incinerators along with other non-hazardous or hazardous waste. The diverse composition of waste toner powder, however, renders them unsuitable for this disposal method as it is difficult to predict what type of pollutants would be emitted in the combustion process. Another disadvantage is the size of the toner particles; they could easily drift along with the flue gases, which can hinder the operation of the treatment facilities.

The data obtained from the composition tests of the four toner samples confirm the presence of the main components - styrene acrylate copolymer, carbon black and iron oxide (black toner), titanium dioxide and amorphous silica. The presence of these ingredients and the high initial temperature of combustion justify the exploration of the possibility for utilising waste toner powder as colorant and filler in synthetic rubber manufacturing. The initial experiments that were carried out show that toners incorporate well into the polymer matrix and they successfully color the final product.

Fig. 13 Samples of synthetic rubber produced with toner powder (cyan, yellow and magenta) used as colorant in raw form and after vulcanisation

The colors remain even after the vulcanisation process performed at 180°C. The fact that toners are non-hazardous waste and pose no risk to the environment and human health allows the application of this rubber in the production of a variety of products.

V. CONCLUSION

The results from the analyses that were carried out can be summarized into the following conclusions:

- Toner powders have a high calorific value – ranging from 2300 to 6170 J/g, which allows disposal through conversion into an energy resource. Incineration of waste toner powder should be carried out under appropriate conditions in incinerators provided with specialized equipment for flue gas treatment.
- Waste toner powder may be used as a filler and as a coloring agent in the rubber industry, i.e. it can be disposed of through conversion into raw material.
- The tribo-chemical production method of toner particles smaller than 10 μm, their application and the specific mechanisms of disposal and impact on the environment and human health allow the implementation of a new scientific direction - "tribo-ecology".

ACKNOWLEDGMENT

This paper has been produced with the financial assistance of the European Social Fund, project number BG051PO001-3.3.06-0014. The author is responsible for the content of this material, and under no circumstances can be considered as an official position of the European Union and the Ministry of Education and Science of Bulgaria.

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