CADMIUM PIGMENTS LISTING BACKGROUND DOCUMENT FOR THE INORGANIC CHEMICAL LISTING DETERMINATION

This Document Contains No Confidential Business Information

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1. SECTOR OVERVIEW

1.1 SECTOR DEFINITION, FACILITY NAME AND LOCATION

Cadmium pigments are made by combining cadmium metal (a saleable mineral product) with acid and sodium sulfide to produce cadmium sulfide. Cadmium sulfide is combined with other chemicals, such as selenium and zinc, to produce different colors for use in paints and pigments. The sole United States cadmium pigments manufacturer is Millennium Specialty Chemicals, Inc., located in Baltimore, Maryland.

1.2 PRODUCTS, PRODUCT USAGE AND MARKETS

Cadmium is a naturally occurring metallic element and is one of the components of the earth's crust.[1] The chemical symbol for cadmium is Cd. Cadmium metal is bluish-white, malleable, ductile, flexible and soft enough to be cut with a knife.[2] Cadmium is recovered primarily through the smelting of zinc. It has an atomic weight of 112.4 g/mol, a melting point of 321^{o} C and a density of 8.64 g/cm^{3}.

Several industrial applications were developed during the first half of the 20th century because of the element's unique chemical and physical properties. Cadmium is used widely in special alloys, pigments, coatings, stabilizers and rechargeable nickel-cadmium batteries. Cadmium metal is used mainly for nickel-cadmium battery production. Approximately 13 percent of the total U.S. consumption of cadmium is used to produce pigments. The pigments usually are produced as powders but are also available in other forms such as pastes and liquids. For applications in the plastics industry, cadmium pigments are available in master batch pellets, which incorporate the pigment in pellets of compounded polymer resins.

Cadmium pigments produce intense colors such as yellow, orange, red, and maroon. They are used in artists' colors, plastics, glasses, ceramics and enamels.[3] Cadmium pigments are insoluble in water and in organic solvents and are resistant to detergents and corrosive alkaline chemicals. Cadmium pigments are stable at high temperatures and remain strong and bright over long periods of time and in the presence of strong sunlight.[4] This is an advantage in the manufacturing of plastics (a process that utilizes extreme heat) and in coating high-temperature surfaces. Cadmium pigments also are useful in plastic applications because of their dispersion, non-migration and non-bleeding properties.

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[1]http://www.jamesmbrown.co.uk/cd_pigments/cadmium.htm

[2]http://www.amm.com/ref/cadm.htm

[3]http://www.jamesmbrown.co.uk/cd_pigments/cadmium.htm

[4]http://www.osha-slc.gov/Preamble/Cadmium_data/CADMIUM8.html

1.3 PRODUCTION

In the RCRA §3007 questionnaire, Millennium Specialty Chemicals, Inc. reported generating approximately 280 metric tons of cadmium pigments in 1998. Imports account for 20 to 30 percent of the U.S. market at the present time.[5]

1.4 PRODUCTION, PRODUCT AND PROCESS TRENDS

The use of cadmium pigments is declining in those applications where less expensive substitutes can be used.[6] Growth in the overall demand for cadmium pigments is limited to those applications requiring their use, such as the plastics industry, where a substitute would not be adequate. The plastics industry is currently the main consumer of cadmium pigments, accounting for about 80 to 90 percent of the total consumption.

Our RCRA §3007 survey results show that six facilities have ceased production of cadmium pigments in recent years. The total demand for cadmium pigments in the next few years is likely to remain stable under current technological conditions.

[5]Ibid

[6]Ibid

2. DESCRIPTION OF MANUFACTURING PROCESS

Millennium Specialty Chemicals, Inc. uses cadmium metal as the raw material in the production process. **Figure 2.1** is a general process flow diagram and may not account for specific process variations. The process can be divided into five steps; the following description refers to wastes that are further characterized in Section 3.

Cadmium Attack Process

The initial reaction involves mixing cadmium metal, nitric acid, sulfuric acid, and water as the reactants that will produce a cadmium sulfate product. The heat of reaction is large and is controlled by the rate at which acid is added. The nitric acid is used to oxidize the cadmium metal. Chemical reagents are added to the liquor to selectively precipitate out metals that are present as impurities. These impurities are the primary components of the iron press residue.

Striking Process

The reaction mixture from the cadmium attack process is used in the striking process. The differentiation between red and yellow pigments occurs in this step. During the striking process, cadmium compounds are precipitated from the initial reaction mixture by the addition of sodium sulfide to the strike tanks. The process yields a slurry that, after filtration, is the first intermediate in pigment production. This intermediate is called the "greencake". The filtering process generates filter cloths which are one component of the contaminated paper and cloth wastestream. Selenium is added to the greencake to produce red pigment. Zinc is added to the greencake to produce yellow pigment. The greencakes are separated from process waters, washed and collected on filter presses. The process wastewater and the rinse liquids are components of the process wastewater from filtering the greencake wastestream. Process wastewater from filtering the greencake wastestream is sent to the onsite pretreatment plant and then to a Publicly Owned Treatment Works (POTW). Discarded filter cartridges generated in this step of the process are a portion of the contaminated paper and cloth wastestream. Dry pigment is collected in the dust collector system and is a portion of the miscellaneous solid waste wastestream.

Calcination and Wet Process

The calcination operation changes the crystal structure of the greencake and gives it the properties of a pigment. This process occurs in a retort heated to a high temperature. Vapors from this process are sent through gas scrubbers and then released to the atmosphere. The wastewater from the gas scrubbing operation contains sodium hydroxide and is a portion of the gas scrubber wastewater wastestream. The calcination process generates contaminated gaskets which are components of the contaminated gaskets wastestream. Filter cloths are generated at this point in the process and are components of the contaminated paper and cloth wastestream. Stack cleanouts and pressed pigment are generated at this point in the process and are a portion of the miscellaneous solid wastes wastestream.

The pigment quality is improved by washing salts and oversized particles from the pigment and reducing

the acid solubility of the cadmium pigment. The wastewater from this process is a portion of the process wastewaters from the wet washing system wastestream. The residue produced in this step, coarse material from wet processing, is a portion of the miscellaneous solid wastes wastestream.

Pigment Drying

The pigment is separated from process water and collected on a filter press where it is washed again. The washed cake is removed from the press and dried in ovens. Two residues produced from this process, filter cloths and filter cartridges, are both portions of the contaminated paper and cloth wastestream. The washwater is a portion of the process wastewaters from wet washing system wastestream.

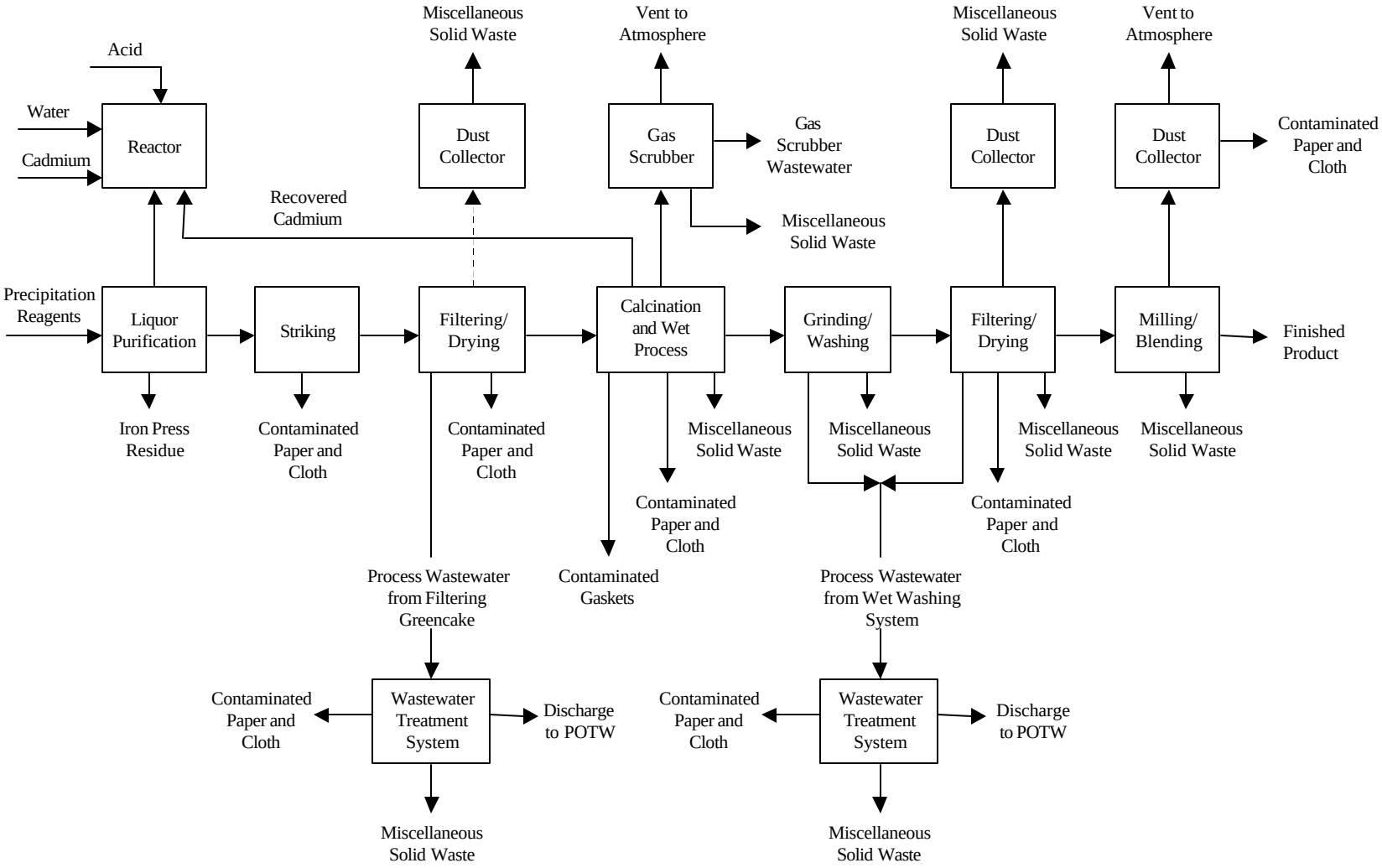
Milling and Blending

In this final step, the dried pigment is made into a grind or a blend. Grinds, or unblended pigments, are pressed and dried and given to the mill operator as a presscake. The blends are pigments that are prepared to specific shades as requested by a customer. The final product contains 20 - 60 percent cadmium. Barium sulfate also may be blended in to the final product to reduce pigment strength. The dry dust produced in this operation is collected and is a portion of the miscellaneous solid wastes wastestream. Dust collector bags are generated as a residual at this point in the process and are a portion of the contaminated paper and cloth wastestream.

Wastewater Pretreatment Process

Wastewaters generated after the calcination process are treated to recover cadmium, which is reintroduced into the cadmium attack process. Gas scrubber water and process wastewater from the greencake filtering process are pH adjusted, and treated to remove cadmium and zinc. These wastewaters are then sent to an onsite closed pretreatment tank for pH adjustment, two-step filtration, and monitoring for turbidity before discharge to a POTW. The filtration processes at the pretreatment plant generate filter cloths, which are a portion of the contaminated paper and cloth wastestream, and filtered pigments, which are the sludge generated from the pretreatment process. The filtered pigments are a portion of the miscellaneous solid wastes wastestream.

Figure 2.1 - Process Flow Diagram for the Production of Cadmium Pigments



3. WASTE GENERATION AND MANAGEMENT

Millennium uses a saleable mineral product as their only feedstock, their process is not be classified as mineral processing; rather Millennium is conducting chemical manufacturing. All waste streams from chemical manufacturing are non-Bevill exempt solid wastes.

This section discusses the wastes generated from the production of cadmium pigments: the wastestreams, the characterization of the wastestreams, current management practices, and our evaluation of the wastes. **Section 3.1** discusses a waste, reported by the facility in its RCRA §3007 questionnaire, that is outside the scope of the Consent Decree. **Section 3.2** presents the non-wastewater wastes. **Section 3.3** details the wastewater wastes. **Appendix A** presents a summary of the wastestreams generated by Millennium Specialty Chemicals Inc. - Baltimore, MD from the production of cadmium pigments, volume of the wastestreams generated in metric tons per year (MT/yr), and the associated final management step.

3.1 DEBRIS

Millennium Specialty Chemicals, Inc., reported one wastestream, contaminated debris, that was generated from excavation activities at the plant. This wastestream, consisting of soil and construction debris, was generated in 1997 as a one-time generation event. EPA considers these types of material to be outside the scope of the Consent Decree.

3.2 NON-WASTEWATER

The non-wastewater category includes miscellaneous solid wastes, contaminated paper and cloth, contaminated gaskets, and iron press residue. **Table 3.1** presents a summary of the non-wastewaters generated at the Millennium Specialty Chemicals Inc., Baltimore, MD facility, waste volumes, and waste management practices.

Table 3.1 - Non-Wastewater Generated from the Production of Cadmium Pigments

Wastestreams	Waste Volume (MT/yr)	Management Practice
Miscellaneous solid wastes	33.5 MT	Each waste is drummed (separately or sometimes combined) and shipped to a commercial off-site hazardous waste treatment facility to be treated and decharacterized before placing in a Subtitle D landfill.
Contaminated paper and cloth	9.3 MT	
Contaminated gaskets	0.3 MT	
Iron press residue	4.5 MT	

In its RCRA §3007 survey, the facility classified all four non-wastewater wastes generated, as characteristic hazardous for barium, cadmium, and selenium. The total volume of these four wastes was 47.6 metric tons in 1998.

3.2.1 Miscellaneous Solid Wastes

Waste Generation

The miscellaneous solid wastes wastestream is generated at various points in the cadmium pigments production process. The waste includes the following materials.

- Stack cleanouts from the gas scrubber and pressed pigment generated during the calcination and wet process production step;
- Salts and oversized particles filtered from the unrefined pigment. These are called "coarse" materials from wet processing;
- Dust from ventilation systems;
- Mill clean-outs;

- Cadmium recovery filtered material;

- Filtered pigment (sludges) generated at the pretreatment plant from pretreatment process.

The miscellaneous solid wastes residual is the largest subcategory of the non-wastewater category. The total amount of residue generated in 1998 was about 33.5 MT.

Waste Characterization

This waste subcategory was characterized in the RCRA §3007 questionnaire response. The generator reported this wastestream to be characteristic hazardous for D005 (Barium), D006 (Cadmium) and D010 (Selenium). There are no other hazardous constituents reported and we have no reason to expect other hazardous constituents to be present in these wastes. The wastestream has a pH of 7.7. **Table 3.2** presents the analytical data provided in the survey characterizing miscellaneous solid wastes, as generated.

Table 3.2 - Characterization of Miscellaneous Solid Wastes

Constituents	Total Concentration (mg/kg)	TCLP Concentration (mg/l)
arsenic	NR	<0.5
barium	210	<5
cadmium	490,000	560
chromium	NR	<0.1
lead	NR	<0.5
mercury	NR	<0.01
selenium	30,000	1.2
silver	NR	<0.05

NR: not reported

3.2.2 Contaminated Paper and Cloth

The contaminated paper and cloth wastestream is generated at several points in the cadmium pigments production process. The waste includes the following materials:

- Spent filter cloths and filter cartridges generated from filtration of the greencake during the striking process;

- Spent filter cartridges from the greencake drying process and the yellow pigment drying process;
- Filter cloths spent for gas scrubbing during the calcination phase of the process;
- Filter cloths used to filter the unrefined pigment generated after calcination;
- Dust collector bags generated from milling of pigments;
- Dust collector bags from a plant vacuum cleaning system;
- Filter bags and filter cloths generated during the filtering steps at the plant's wastewater pretreatment facility.

The contaminated paper and cloth wastestream is the second largest subcategory of the non-wastewater category. The total amount of this waste generated in 1998 was about 9.3 MT.

Waste Characterization

This waste category was characterized in the RCRA §3007 questionnaire response. The generator reported this wastestream to be characteristic hazardous for D005 (Barium), D006 (Cadmium) and D010 (Selenium). There are no other hazardous constituents reported and we have no reason to expect other hazardous constituents to be present in these wastes. This wastestream has a pH of 8.7. **Table 3.3** presents the analytical data provided in the survey characterizing contaminated paper and cloth, as generated.

Table 3.3 - Characterization of Contaminated Paper and Cloth

Constituents	**TCLP Concentration (mg/l)**
arsenic	<0.5
barium	<5
cadmium	4.5
chromium	<0.1
lead	<0.5
mercury	<0.01
selenium	<0.5
silver	<0.05

3.2.3 Contaminated Gaskets

Waste Generation

The contaminated gaskets wastestream is produced at the calcination step in the cadmium pigments production process. The total amount of this waste generated in 1998 was about 0.3 MT.

Waste Characterization

This waste subcategory was characterized in the RCRA §3007 questionnaire response. The generator reported this wastestream to be characteristic hazardous for D005 (Barium), D006 (Cadmium) and D010 (Selenium). There are no other hazardous constituents reported and we have no reason to expect other hazardous constituents to be present in these wastes. This wastestream has a pH of 10. **Table 3.4** presents the analytical data provided in the survey characterizing contaminated gaskets, as generated.

Table 3.4 - Characterization of Contaminated Gaskets

Constituents	**TCLP Concentration (mg/l)**
arsenic	<0.5
barium	<5
cadmium	2.6
chromium	0.1
lead	<0.5
mercury	<0.01
selenium	<0.5
silver	<0.05

3.2.4 Iron Press Residue

Waste Generation

Iron press residue is generated during the cadmium attack process when chemical reagents are added to the liquor to selectively precipitate out metals that are present as impurities. The total amount of

residue generated in 1998 was about 4.5 MT.

Waste Characterization

This waste subcategory was characterized in the RCRA §3007 questionnaire response. The generator reported this wastestream to be characteristic hazardous for D005 (Barium), D006 (Cadmium) and D010 (Selenium). There are no other hazardous constituents reported. The wastestream has a pH of 9.0. **Table 3.5** presents the analytical data provided in the survey characterizing the iron press residue, as generated.

Table 3.5 - Characterization of Iron Press Residue

Constituents	Total Concentration (mg/kg)	TCLP Concentration (mg/l)
arsenic	NR	<0.5
barium	77	<5
cadmium	96,000	2,600
chromium	NR	0.2
lead	NR	<0.5
mercury	NR	<0.01
selenium	32,000	2.5
silver	NR	<0.05

NR: not reported.

3.2.5 Non-Wastewater Management

Data provided by the facility[7] shows that, over the past seven years, the generator has managed all its non-wastewater residuals from the production of cadmium pigments as TC hazardous wastes. These wastes are placed in drums and shipped with manifests to a commercial off-site Subtitle C facility for treatment. The off-site treatment includes mixing and treating the wastes with other solid wastes and the addition of lime and fly ash to meet the current LDR treatment standards (via stabilization). The resultant mixture forms a concrete-like residue which is managed in a Subtitle D landfill. The landfill is equipped with a daily cover, a leachate collection system, a runoff control system, and groundwater monitoring.

[7]Millennium's April 12, 1999 written response and April 23 email response to our additional information requests.

The historical groundwater information and leachate data provided by the local and state governments [8] indicate that the groundwater monitoring system has been in place since 1993 and that the constituents detected in the landfill leachates are not attributable to the cadmium pigments production wastes. The landfill is closely monitored by the local and state governments[9]. The landfill is subject to a hydrogeologic monitoring plan stipulated by the local government, which requires the landfill facility to sample leachate four times a year[10]. Leachate samples are collected and analyzed quarterly for parameters that are specified by the County in the Hydrogeologic Monitoring Plan for the landfill, including metals, other inorganic parameters, and volatiles.

3.3 WASTEWATERS

The wastewaters are: gas scrubber wastewaters, process wastewater from filtering the greencake, and process wastewaters from the wet washing system. **Table 3.6** summarizes the wastewaters, waste volumes, and waste management practices.

Table 3.6 - Wastewaters Generated from the Production of Cadmium Pigments

Waste Categories/Types	Waste Volumes	Management Practice	
Gas scrubber wastewater (spent caustic from scrubbing vapors generated from calcination process)	not reported	pH adjusted, treated to remove zinc and cadmium. The resulting sludge is a portion of the miscellaneous solid wastes wastestream.	All these wastewaters then are combined and further treated in on-site closed tanks for pH adjustment; 2-step filtration; monitoring for turbidity prior to discharge to a POTW
Process wastewater from filtering the greencake	not reported		
Process wastewaters from wet washing system	not reported	pH adjusted, treated to recover cadmium	

[8] Quarterly leachate monitoring data collecting during March 95 to September 98, provided by Michigan's Dept. of Environment, Wayne County District Office and Local Office.

[9]Weekly inspection reports by Wayne County Dept of Environment about the Sauk Trail Hills opertions and compliance from April 2, 1997 to April 7, 1999.

[10]An approval letter dated March 24, 1999 from the Michigan Dept. of Environmental Quality to the Sauk Trail Hills Landfill in Wayne County, MI for their application of renewal operating license. Valid date: March 22, 1999 to March 22, 2001.

3.3.1 Gas Scrubber Wastewater

Waste Generation

Gas scrubber wastewater is generated from spent caustic used to scrub vapors generated during the calcination step of the cadmium pigments production process. The calcination process occurs in a retort and the vapors from this process are sent through gas scrubbers. The facility did not report the generation volume for this wastestream.

Waste Characterization

This waste subcategory was characterized in the RCRA §3007 questionnaire response. This wastestream is not a hazardous waste. It has a pH greater than 11 and contains low levels of cadmium (0.02 to 1.0 ppm) and selenium (0.02 to 3.0 ppm).

3.3.2 Process Wastewater from Filtering the Greencake

Waste Generation

The process wastewater wastestream from filtering the greencake is generated after the striking process when the wastewaters are separated from the greencake.

Waste Characterization

The facility did not characterize this wastestream in the RCRA §3007 questionnaire.

3.3.3 Process Wastewaters From Wet Washing System

Waste Generation

Process wastewaters from the wet washing system are produced at two points in the process: when the pigment quality is improved by removing salts and oversized particles and after the pigment drying step when the pigment is collected on a filter press and washed.

Waste Characterization

The facility did not characterize this wastestream in the RCRA §3007 questionnaire.

APPENDIX A

Summary of Waste Generation and Management

Wastestreams	Waste Volume (MT/yr in 1997)	Final Waste Management Step
Miscellaneous solid wastes	33.5	Offsite Subtitle D landfill
Contaminated paper and cloth	9.3	Offsite Subtitle D landfill
Contaminated gaskets	0.3	Offsite Subtitle D landfill
Iron Press residue	4.5	Offsite Subtitle D landfill
Gas scrubber wastewaters	NR	Treated on-site in closed tanks for pH adjustment; 2-step filtration; monitoring for turbidity prior to discharge to a POTW
Process wastewater from filtering the greencake	NR	Treated on-site in closed tanks for pH adjustment; 2-step filtration; monitoring for turbidity prior to discharge to a POTW
Process wastewaters from wet washing system	NR	Treated on-site in closed tanks for pH adjustment; 2-step filtration; monitoring for turbidity prior to discharge to a POTW

NR = not reported in RCRA §3007 questionnaire