

Physico-chemical testing recommendations for refinables substances

Introduction

In order to complete a full physico-chemical dataset for the refinables which are undergoing upgrades to full substance registrations, additional data are required for some substances. For the original registrations in 2010, the physico-chemical endpoints were completed by testing conducted at Harlan on a representative sample of each refinable. Transformation/dissolution tests also were conducted for each refinable that was registered in 2010 at >1000 tpa (tonnes per annum) and the results from these tests were used to fill the water solubility endpoint. Novel testing is proposed to complete the remaining physico-chemical endpoints which cannot be waived for those refinables where a complete set of physico-chemical tests were not conducted in 2010. Refinables which are not undergoing an upgrade to full substance registration have not been considered in this report.

Data requirements

In 2010, all refinables were considered to be intermediates under strictly controlled conditions (SCC). Those which were registered as intermediates under SCC at greater than 1000 tpa required a full Annex VII dataset, whereas those being registered as intermediates under SCC at less than 1000 tpa only required available data. Therefore, for those refinables being registered at <1000 tpa, physico-chemical testing was only conducted for those endpoints required for classification purposes. Now that the dossiers are being upgraded to full substance dossiers, additional endpoints need to be filled in order to meet the REACH registration requirements.

The Annex VII physico-chemical endpoints which need to be completed are: appearance, melting point, boiling point, density, vapour pressure, granulometry, water solubility, partition coefficient, surface tension, flash point, flammability, auto-flammability, explosive properties and oxidising properties. There are no additional physico-chemical endpoints required under Annex VIII. Under Annex IX, stability in organic solvents, dissociation constant and viscosity are also required.

Information provided recently by the PMRC indicated that slags and slimes & sludges are currently under discussion and may be split into separate substances. For the purposes of this recommendation they have been included as single substances as previously described. When a decision is reached on whether they are to be split, the resulting substance(s) will be addressed separately.

Data gap matrices

Data gap matrices are presented in Tables 1A and 1B, showing how each endpoint was completed for the 2010 registration deadline and where there are now gaps for the registration upgrade. The REACH required endpoints are listed by Annex on the left hand side. The information requirements for each substance are listed across the top, with those substances being upgraded to >1000 tpa substances requiring completion of Annex VII to X

endpoints, those upgraded to 100-1000 tpa substances requiring Annex VII to IX and those upgrading to 10-100 tpa requiring Annex VII and VIII.

Table 1A. Data matrix for substances with full Annex VII physico-chemical datasets

Substances	Annex	Dore	Slags, PM refining	Slimes and sludges, PM refining	Matte leaching residue	Matte, PM refining	Materials for reclaim, PM with or without support
Data requirements		Annex X	Annex X	Annex X	Annex X	Annex IX	Annex IX
Appearance	7	Brown and silver granules (Harlan 2010) Grey liquid (Aurubis 2010)	Green solid (Harlan 2010) Green solid (Umicore 2010)	Black solid (Harlan 2010) Grey powder (Aurubis 2010) Yellow powder (Aurubis 2010)	Grey powder (Harlan 2010) Black powder (Umicore 2010)	Grey solid (Harlan 2010) Black solid (Umicore 2010)	Grey powder (Harlan 2010) Beige powder (JM 2010)
Melting point	7	>450°C (Harlan 2010)	>450°C (Harlan 2010)	>450°C (Harlan 2010)	>450°C (Harlan 2010)	>450°C (Harlan 2010)	>450°C (Harlan 2010)
Boiling point ^A	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Density	7	10.8 (Harlan 2010)	2.75 (Harlan 2010)	2.03 (Harlan 2010)	3.39 (Harlan 2010)	4.18 (Harlan 2010)	2.96 (Harlan 2010)
Granulometry ^B	7	0.449% <100 µm (Harlan 2010)	14.7% <100 µm (Harlan 2010)	Waiver	57.2 % <100 µm (Harlan 2010)	9.26% >100 µm (Harlan 2010)	99.8% <100 µm (Harlan 2010)
Vapour pressure ^C	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Partition coefficient ^D	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Water solubility ^E	7	T/D results	T/D results	T/D results	T/D results	T/D results	T/D results
Surface tension ^F	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Flash point ^G	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Auto-flammability ^I	7	Waiver. >400°C (Harlan 2010)	Waiver. >400°C (Harlan 2010)	Waiver. >400°C (Harlan 2010)	Waiver. 265°C (Harlan 2010)	Waiver. >400°C (Harlan 2010)	Waiver. >400°C (Harlan 2010)
Flammability ^J	7	Waiver	Waiver	Not flammable (Harlan 2010)	Not flammable (Harlan 2010)	Not flammable (Harlan 2010)	Not flammable (Harlan 2010)
Explosiveness	7	Waiver ^K	Waiver ^K	Waiver ^L	Waiver ^K	Waiver ^K	Waiver ^K
Oxidising properties	7	Waiver ^M	Waiver ^N	Waiver ^O	Waiver ^P	Waiver ^Q	Waiver ^R
Stability in organic solvents	9	Data gap	Data gap	Data gap	Data gap	Data gap	Data gap
Dissociation constant	9	Data gap	Data gap	Data gap	Data gap	Data gap	Data gap
Viscosity	9	Data gap	Data gap	Data gap	Data gap	Data gap	Data gap

Table 1B. Data matrix for substances with Annex VII physico-chemical data gaps

Substances	Annex	Ag electrolyte	Flue dust, PM refining	Residues cementation and reduction, PM refining	Materials for reclaim, PM on bricks, crucibles, trays etc	Materials for reclaim, PM production by-products	Lead bullion, PM metal rich
Data requirements		Annex X	Annex IX	Annex IX	Annex IX	Annex IX	Annex VIII
Appearance	7	Blue liquid (Harlan 2010)	Grey powder (Harlan 2010) Grey powder (JM 2010)	Black powder (Harlan 2010) Brown powder (Heraeus 2010)	Grey solid (Harlan 2010) Grey powder (JM 2010)	Grey powder (Harlan 2010) Brown powder (JM 2010)	Solid (Vale 2010)
Melting point	7	No data	>450°C (Harlan 2010)	>450°C (Harlan 2010)	>450°C (Harlan 2010)	>450°C (Harlan 2010)	No data
Boiling point ^A	7	No data	No data	No data	No data	Waiver	No data
Density	7	No data	No data	No data	No data	No data	No data
Granulometry	7	No data	No data	No data	No data	No data	No data
Vapour pressure ^C	7	No data	No data	No data	No data	Waiver	No data
Partition coefficient ^D	7	No data	No data	No data	No data	Waiver	No data
Water solubility ^E	7	No data	No data	No data	T/D results	T/D results	T/D results
Surface tension ^F	7	No data	No data	No data	No data	Waiver	No data
Flash point	7	>Boiling Point (Harlan 2010)	No data	No data	No data	Waiver	No data
Auto-flammability	7	>400°C (Harlan 2010)	>400°C (Harlan 2010)	>400°C (Harlan 2010)	>400°C (Harlan 2010)	>400°C (Harlan 2010)	No data
Flammability	7	Waiver ^H	No data	Not flammable (Harlan 2010)	Waiver ^J	Not flammable (Harlan 2010)	No data
Explosiveness	7	Waiver ^K	Waiver ^L	Waiver ^L	Waiver ^K	Waiver ^L	No data
Oxidising properties	7	No oxidising (Harlan 2010)	No data	Waiver ^Q	Waiver ^R	Waiver ^Q	No data
Stability in organic solvents	9	No data	No data	No data	No data	No data	Not required
Dissociation constant	9	No data	No data	No data	No data	No data	Not required
Viscosity	9	No data	No data	No data	No data	No data	Not required

^A In accordance with column 2 of REACH Annex VII, the boiling point study does not need to be conducted as this substance is a solid which melts above 300°C.

^B In accordance with column 2 of REACH Annex VII, the granulometry study does not need to be conducted as the substance is marketed or used in non solid or granular form.

^C In accordance with column 2 of REACH Annex VII, the vapour pressure study does not need to be conducted as this substance has a melting point above 300°C.

^D In accordance with column 2 of REACH Annex VII, the partition coefficient study does not need to be conducted as this substance is inorganic.

^E Water solubility testing is not appropriate for complex metal and sparingly soluble metals and metal compounds. Transformation dissolution testing has been conducted and is presented in section 5.6.

^F In accordance with column 2 of REACH Annex VII, the surface tension study does not need to be conducted as, based on the structure of this substance, surface activity is not expected or predicted and surface tension is not a desired property of the material.

^G In accordance with column 2 of REACH Annex VII, the flash point study does not need to be conducted as this substance is inorganic.

^H The primary value for ease of ignition is flash point. Ag Electrolyte is not a flammable liquid and does not exhibit a flash point at any temperature up to its boiling point (see section 4.11).

^I In accordance with column 2 of REACH Annex VII, the self-ignition temperature study does not need to be conducted as the substance is a solid and preliminary results exclude self-heating of the substance up to 400°C.

^J In accordance with REACH Annex XI, testing for flammability is scientifically unjustified since the substance is a solid form containing only metals and is not manufactured or available as a powder form.

^K In accordance with column 2 of REACH Annex VII, the explosive properties study does not need to be conducted as there are no chemical groups associated with explosive properties present in the molecule.

^L According to expert judgement there are no chemical groups within the test items composition that would imply explosive properties.

^M The main components of the test item do not contain oxygen or halogen atoms. Therefore, the oxidising properties of the test item can be predicted negative.

^N The test item structure contains oxygen. According to the guidance given in appendix 6 section 6 of the United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, testing is required if the test item contains oxygen. However, the oxygen in silicate and carbonates is not readily available for oxidation and the metal oxides present are generally in small amounts or are known to be nonoxidising. Therefore, the oxidising properties of the test item can be predicted negative.

^O The test item contains oxygen. According to the guidance given in Appendix 6, section six of the United Nations Recommendations on the Transport of Dangerous Goods Manual of Tests and criteria, testing is required if the test item contains oxygen and /or halogens. The oxygen is present as sulphate and therefore the oxygen is not readily available for oxidation. The metal oxides and chlorides present are generally in small amounts or are known to be non-oxidising. Therefore, the oxidising properties of the test item can be predicted negative.

^P The test item contains oxygen. According to the guidance given in Appendix 6, section six of the United Nations Recommendations on the Transport of Dangerous Goods Manual of Tests and criteria, testing is required if the test item contains oxygen. The oxygen is bonded to silicone or is present as sulphate or hydroxide and therefore the oxygen is not readily available for oxidation. The metal oxides present are generally in small amounts or are known to be non-oxidising. Therefore, the oxidising properties of the test item can be predicted negative.

^Q The main components of the test item do not contain oxygen or halogen atoms. The metal oxides present are generally in small amounts or are known to be non-oxidising. Therefore, the oxidising properties of the test item can be predicted negative.

^R In accordance with column 2 of REACH Annex VII, the oxidising properties study does not need to be conducted as the substance is incapable of reacting exothermically with combustible materials on the basis of its chemical structure.

Methods for completing endpoints

Waivers

Waivers can be applied to fill a number of the physico-chemical endpoints. The partition coefficient endpoint can be waived on the basis that the substances are inorganic. Flash point studies are only required for liquids and therefore this endpoint will be waived for solid substances. Conversely, the flammability and granulometry endpoints are only required for the solid refinable substances and therefore will be waived for those which are liquids. Surface tension can be waived on the basis of the structure of the substances.

Where melting point was tested for refinables as part of the 2010 registrations, these are all greater than 450°C and therefore the boiling point and vapour pressure endpoints have been waived on the basis of the melting point being above 300°C. It is expected that the melting point for the other refinables will also be >300°C and therefore the boiling point and vapour pressure waivers could also be applied for these substances.

One potential option for completing the oxidising properties endpoint is waiving the endpoint on the basis of the substance's chemical structure. This waiver was applied for some refinables as part of the 2010 registration process, as identified in the footnotes to tables 1A and 1B. Two substances currently have a data gap for the oxidising properties endpoint and the Refinables Working Group would need to confirm whether the oxidising properties endpoint can be waived for these substances as well. As flue dust, PM refining potentially contains high concentrations of various metal oxides and/or hydroxides, the waiver on the basis of chemical structure may not be appropriate and an oxidising properties test may be required.

One refinable, lead bullion, PM metal rich, has a data gap for the explosive properties endpoint. This endpoint may be waived on the basis that the substance contains no chemical groups associated with explosive properties. The Refinables Working Group would need to confirm whether the explosive properties endpoint can be waived for this substance.

Three Annex IX physico-chemical endpoints are required for upgrades to substance registrations greater than 100 tpa (all refinables substances apart from lead bullion, PM metal rich). As Annex IX endpoints were not considered to be required for any of the refinables when they were registered in 2010, these endpoints are data gaps for all substances. It is proposed that the dissociation constant endpoint is waived on the basis that the refinable substances do not contain any functional groups which dissociate. The stability in organic solvents endpoint can be waived as the refinable substances are inorganic. For the solid refinable substances viscosity can be waived, though testing is proposed for Ag electrolyte as a liquid.

Testing recommendations

Water solubility and transformation/dissolution

The water solubility endpoint has been completed where appropriate as part of the 2010 registrations with the statement: "Water solubility testing is not appropriate for complex

metal and sparingly soluble metals and metal compounds. Transformation dissolution testing has been conducted and is presented in section 5.6”.

Following the same procedure for the remaining substances, it is proposed that any refinables without data undergo transformation/dissolution testing. Although the physico-chemical endpoint which needs to be completed is the water solubility of the substances, this information is not directly relevant to complex and sparingly soluble metals and metal compounds. As the substances do not have a defined composition as such, water solubility studies are not appropriate as it is not possible to measure a single dissolved concentration representative of the substance. Therefore, it is proposed instead to conduct Transformation/Dissolution studies where required.

Other physico-chemical endpoints

Testing is recommended for melting point, density, granulometry, auto flammability, flammability, oxidising properties and viscosity for some of the refinable substances, as indicated in Tables 2A and 2B.

It is recommended that the testing is conducted in a tiered manner, with melting point tests conducted first and, if the melting point is found to be <300°C, the boiling point and vapour pressure tests would then be conducted.

Table 2A. Recommendations for substances with full Annex VII physico-chemical datasets

Substances	Annex	Dore	Slags, PM refining	Slimes and sludges, PM refining	Matte leaching residue	Matte, PM refining	Materials for reclaim, PM with or without support
Data requirements		Annex X	Annex X	Annex X	Annex X	Annex IX	Annex IX
Appearance	7	Data available	Data available	Data available	Data available	Data available	Data available
Melting point	7	Data available	Data available	Data available	Data available	Data available	Data available
Boiling point	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Density	7	Data available	Data available	Data available	Data available	Data available	Data available
Granulometry	7	Data available	Data available	Waiver	Data available	Data available	Data available
Vapour pressure	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Partition coefficient	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Water solubility	7	T/D results	T/D results	T/D results	T/D results	T/D results	T/D results
Surface tension	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Flash point	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Auto-flammability	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Flammability	7	Waiver	Waiver	Data available	Data available	Data available	Data available
Explosiveness	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Oxidising properties	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver
Stability in organic solvents	9	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed
Dissociation constant	9	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed
Viscosity	9	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed

Table 2B. Recommendations for substances with Annex VII physico-chemical data gaps

Substances	Annex	Ag electrolyte	Flue dust, PM refining	Residues cementation & reduction, PM refining	Materials for reclaim, PM on bricks, crucibles, trays etc	Materials for reclaim, PM production by-products	Lead bullion, PM metal rich
Data requirements		Annex X	Annex IX	Annex IX	Annex IX	Annex IX	Annex VIII
Appearance	7	Data available	Data available	Data available	Data available	Data available	Data available
Melting point	7	TEST	Data available	Data available	Data available	Data available	TEST
Boiling point	7	Test dependent on melting point	Waiver proposed	Waiver proposed	Waiver proposed	Waiver	Test dependent on melting point
Density	7	TEST	TEST	TEST	TEST	TEST	TEST
Granulometry	7	TEST	TEST	TEST	TEST	TEST	TEST
Vapour pressure	7	Test dependent on melting point	Waiver proposed	Waiver proposed	Waiver proposed	Waiver	Test dependent on melting point
Partition coefficient	7	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver	Waiver proposed
Water solubility	7	T/D test proposed	T/D test proposed	T/D test proposed	T/D results available	T/D results available	T/D results available
Surface tension	7	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver	Waiver proposed
Flash point	7	Data available	Waiver proposed	Waiver proposed	Waiver proposed	Waiver	Waiver proposed
Auto-flammability	7	Data available	Data available	Data available	Data available	Data available	TEST
Flammability	7	Waiver	TEST	Data available	Waiver	Data available	TEST
Explosiveness	7	Waiver	Waiver	Waiver	Waiver	Waiver	Waiver proposed
Oxidising properties	7	Data available	TEST dependent on waiver	Waiver	Waiver	Waiver	TEST
Stability in organic solvents	9	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Not required
Dissociation constant	9	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Not required
Viscosity	9	TEST	Waiver proposed	Waiver proposed	Waiver proposed	Waiver proposed	Not required
Transformation/ Dissolution		TEST	TEST	TEST	Data available	Data available	Data available

Information on testing

Based on our previous experience conducting testing at Harlan in 2011-2012, we estimate a four week lead in time with six to eight weeks to conduct and report the recommended physico-chemical testing. This would mean that testing would not be completed for at least three months from the signing of the contract. Table 3 provides estimated costs and timescales for the required physico-chemical tests.

Table 3. Testing information

Endpoint	Test	Lead in time	Estimated timeline	Estimated cost per test	Sample volume	Comments
Melting point	OECD 102	4 weeks	6 – 8 weeks	£1,000.00	1 g / 50 mL	
Boiling point	OECD 103	4 weeks	6 – 8 weeks	£1,000.00	1 g / 50 mL	Not required if melting point >300°C
Density	OECD 109	4 weeks	6 – 8 weeks	£1,000.00	50 g / 50 mL	
Granulometry	OECD 110	4 weeks	6 – 8 weeks	£3,000.00	15 g	
Vapour pressure	OECD 104	4 weeks	6 – 8 weeks	£3,000.00	10 g / 30 mL	Not required if melting point >300°C
Auto-flammability	A16 (solid)	4 weeks	6 – 8 weeks	£2,500.00	50 g / 50 mL	
Flammability	A10 (solid)	4 weeks	6 – 8 weeks	£1,000.00	35 g / 150 g	
Oxidising properties	A17 (solid)	4 weeks	6 – 8 weeks	£3,500.00	300 g	
Viscosity	OECD 114	4 weeks	6 – 8 weeks	£2,000.00	50 mL	Only required for liquids

The estimates provided here are all ball-park figures based on experience conducting tests at Harlan over the last few years and are given here for information. Quotes will need to be collected from the appropriate Contract Research Organisations for official estimates. Please note that these costs relate to the conduct of studies only and do not cover study monitoring.

Following the same procedure as was used for the 2010 registrations, it is proposed that the Transformation/Dissolution tests are undertaken at ECTX. Given the timescales involved during the testing under the 2010 registration program, it is likely that these tests would take six to eight months, which may impact on any proposed timescales for this project. Previously these tests were commissioned and monitored by the PMRC.

Summary of testing recommendations

The physico-chemical tests recommended for each refinable substance are presented in Table 4.

Table 4. Testing recommendations

Substance	Melting point	Boiling point ¹	Vapour pressure ¹	Density	Granulometry	Auto-flammability	Flammability	Transformation/ Dissolution	Oxidising properties	Viscosity
Ag electrolyte	X	(X)	(X)	X	X			X		X
Flue dust				X	X		X	X		
Residues cementation and reduction, PM refining				X	X			X		
Materials for reclaim, PM on bricks, crucibles, trays etc				X	X					
Materials for reclaim, PM production by-products				X	X					
Lead bullion, PM metal rich	X	(X)	(X)	X	X	X	X		X	

¹ Dependent on result of melting point test. If melting point is >300°C this endpoint can be waived