

# High Production Volume (HPV) Challenge Program

## Revised Test Plan for

Petroleum Oxidates and Derivatives Thereof  
Category

Prepared By:

The Lubrizol Corporation  
29400, Lakeland Blvd.  
Wickliffe, OH 44092

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## 1.0 Introduction

On November 30, 2000, the Lubrizol Corporation committed to provide basic toxicity information on chemicals listed under the Environmental Protection Agency (EPA) High Production Volume (HPV) Chemical Challenge Program. The eight sponsored chemicals addressed in this test plan are:

- 64742-98-9 Distillates (petroleum), oxidized light
- 64743-00-6 Hydrocarbon waxes (petroleum), oxidized
- 64743-01-7 Petrolatum (petroleum), oxidized
- 68425-34-3 Petrolatum (petroleum), oxidized, Ca salt
- 68602-85-7 Hydrocarbon waxes (petroleum), oxidized, Me esters
- 68603-10-1 Hydrocarbon waxes (petroleum), oxidized, Me esters, Ba salts
- 68603-11-2 Hydrocarbon waxes (petroleum), oxidized, Me esters, Ca salts
- 68603-12-3 Hydrocarbon waxes (petroleum), oxidized, Me esters, Na salts

The process of evaluating the members of the “Petroleum Oxidates and Derivatives Thereof” category entailed the following stepwise process:

- grouping of chemicals into a putative category
- gathering relevant data for each member of the category
- evaluating the physico-chemical, environmental, aquatic, and health effect patterns to confirm adequacy of category
- construction of a matrix of SIDS endpoints for category members
- identification of data gaps for critical endpoints within the category

## 2.0 Development of Oxidates and Derivatives thereof Category

The HPV Challenge Program encourages the development of chemical categories as an economic, animal sparing, and efficient way to complete the program goals. The EPA guidance document, Development of Chemical categories states, “a chemical category is a group of chemicals whose physicochemical and toxicological properties are likely to be similar or follow a regular pattern as a result of structural similarity. The similarities should be based on a common functional group, common precursors or breakdown products (resulting in structurally similar chemical) and an incremental and constant change across the category.” A goal of this category analysis document is to use interpolation and/or extrapolation to untested members to reduce the amount of additional testing needed to complete the SIDS requirements.

### 2.1 Chemical identity

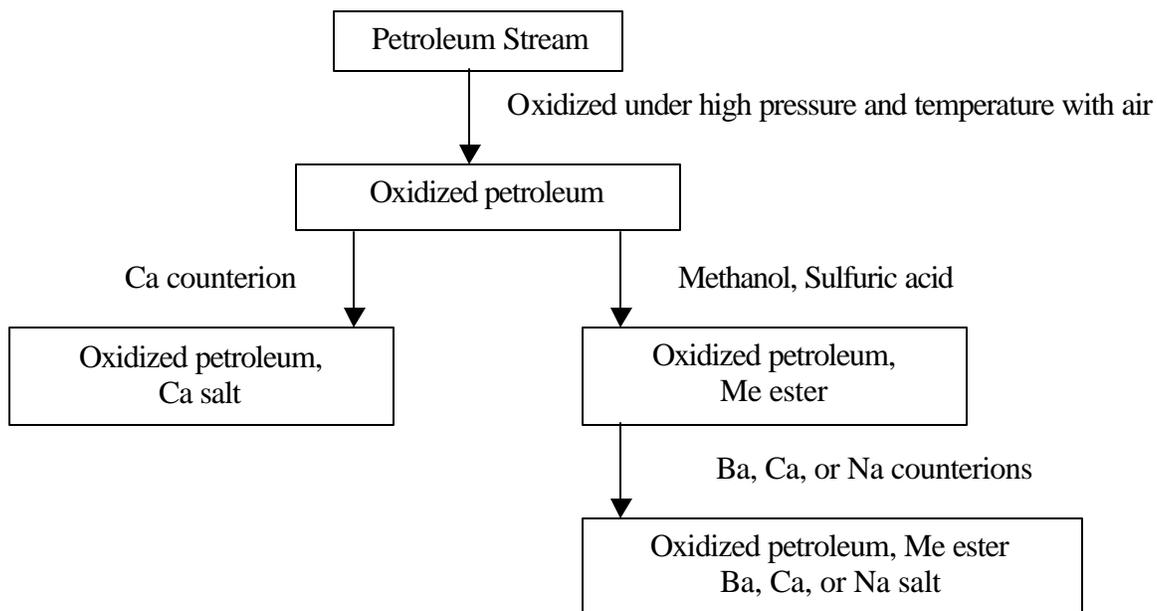
The members of this test plan are petroleum oxidates, oxidized methyl esters, and their salts, which are derived from aliphatic hydrocarbons. The petroleum oxidates vary in molecular weight, which is determined by the starting raw material and the extent of oxidation. The petroleum oxidates described in this test plan are derived from slack wax, petrolatum, or petroleum distillate. The slack wax and petrolatum starting materials range in chain length from C33 to C43 while the petroleum distillate starting material ranges in chain length from C9-C16. There are distinct differences between the petroleum oxidates derived from the slack wax or petrolatum and the light petroleum distillate. These differences

become apparent when comparing their physicochemical properties. Due to the apparent differences in physicochemical properties between the oxidates derived from the slack wax or petrolatum and the oxidates derived from the petroleum distillate, the members of this test plan are divided into two subcategories. Subcategory 1 contains the light oxidized distillate (64742-98-9) derived from the lower molecular weight petroleum distillate. Subcategory 2 contains the petroleum oxidates and derivatives (64743-00-6, 64743-01-7, 68425-34-3, 68602-85-7, 68603-10-1, 68603-11-2, 68603-12-3) derived from the higher molecular weight slack wax and petrolatum.

All of the petroleum oxidates described in this test plan are produced by controlled, liquid phase, partial oxidation using atmospheric air as the oxygen source. Oxidation of the petroleum hydrocarbon is an exothermic reaction, performed under high temperature and pressure.

The typical composition of the petroleum oxidate in subcategory 1 is 50% unreacted petroleum starting material, 10% carboxylic acid (mono- and di-), 25% ketone, the remainder of the composition consists of oxyacids, aldehydes, and methyl ester. The typical composition of the petroleum oxidates in subcategory 2 (64743-01-7 and 64743-00-6) is 40-50% unreacted petroleum starting material, 30-35% monocarboxylic acid, the remainder of the composition consists of dicarboxylic acids, oxyacids, aldehydes, and ketones. The oxidized methyl ester, 68602-85-7, is created by an esterification reaction of the petroleum oxidate using methanol and sulfuric acid. The product of this reaction is a mixture of methyl esters, unreacted starting material, mono and di- carboxylic acids, oxyacids, aldehydes, and ketones. The oxidized petroleum or the oxidized methyl ester intermediates are reacted with Ba, Ca, and Na counterions to form the oxidized salt. The counterions act to neutralize the carboxylic acid functional groups. The typical production process is shown in figure 1.

Figure 1 Production process for oxidate derivatives



## 2.2 Uses of Petroleum Oxidates and Derivatives Thereof

The properties of the oxidates and their derivatives that make them useful are their ability to repel and displace water. They have excellent lubricity and corrosion protection properties. The oxidates 64742-98-9, 64743-01-7, and 64743-00-6 are used primarily as intermediates. The salt derivatives and the methyl ester derivatives are useful in preparing oil soluble and water dispersing soaps. These soaps are applied to coiled steel and steel sheets to prevent corrosion before receiving a final paint. They are also used as rust preventatives in a variety of other applications. The petroleum oxidates can be used to replace natural fats and oils in the formulation of cutting, drawing, and rolling oils.

## 3.0 Physical and Chemical Properties

The light petroleum oxidate in subcategory 1 is a liquid at room temperature. The petroleum oxidates and derivatives in subcategory 2 are solids or waxy solids at room temperature. The difference in the physical state of the member in subcategory 1 is due to its variation in carbon chain length of the starting material and the oxidation products. This also accounts for its difference in melting point, boiling point, vapor pressure, octanol water coefficient, and water solubility in comparison to the members in subcategory 2. The differences in the physicochemical properties between the members of subcategory 1 and 2 justifies separating these materials into two separate subcategories.

### 3.1 Melting Point

There is melting point data available for seven of the eight members of this test plan (Table 1). The melting point for the light petroleum oxidate in subcategory 1 is - 31.03 deg C. The melting point for the petroleum oxidates and derivatives in subcategory 2 range from 33.64 to 49.87 deg. C. The untested member 68603-12-3, oxidized Me ester Na salt, is expected to have a melting point similar to 68603-10-1 and 38603-11-2, the oxidized Me ester Ba salt and Ca salt respectively. There is sufficient melting point data available for the members of this test plan; therefore, additional testing is not required.

### 3.2 Boiling Point Range

There is boiling point range data available for seven of the eight members of this test plan (Table 1). The petroleum oxidate in subcategory 1 has a boiling point range of 196 to 842 deg F. The petroleum oxidates and derivatives in subcategory 2 have a boiling point range from 379 to >1200 deg F. The untested member 68603-12-3, oxidized Me ester Na salt, is expected to have a boiling point range similar to 68603-10-1 and 38603-11-2, the oxidized Me ester Ba salt and Ca salt respectively. There is sufficient boiling point data available for the members of this test plan; therefore, additional testing is not required.

### 3.3 Vapor Pressure

There is vapor pressure data available for seven of the eight members of this test plan (Table 1). The petroleum oxidate in subcategory 1 has a vapor pressure of 69 Pa at 25 deg C. The petroleum oxidates and derivatives in subcategory 2 have a

vapor pressure less than 1Pa at 25 deg C. The untested member 68603-12-3, oxidized Me ester Na salt, is expected to have a vapor pressure similar to 68603-10-1 and 38603-11-2, the oxidized Me ester Ba salt and Ca salt respectively. There is sufficient vapor pressure data available for the members of this test plan; therefore, additional testing is not required.

### **3.4 Partition Coefficient**

The octanol water partition coefficient could not be measured for the members of this test plan using OECD guideline 107. This test method would not accurately depict the octanol water coefficient of the members of this category because they are Class 2 substances containing a mixture of hydrophilic and hydrophobic materials. The hydrophilic acids partitioned into the water phase while the hydrophobic, aliphatic hydrocarbons and methyl esters partitioned into the octanol phase giving a distorted value for the octanol water partition coefficient. Due to the complex composition of these materials, a definitive octanol water partition coefficient value can not be made. The calculated octanol water coefficient for the raw material, light petroleum distillate, is 3.3 to 7.06 (ASTDR, 1995). The petroleum oxidate in subcategory 1 is expected to have a similar octanol water partition coefficient to this starting raw material. The members in subcategory 2 are expected to have an octanol water partition coefficient similar to that of their starting materials. The HPV test plan for waxes and related materials indicates that petrolatum and slack wax have an octanol water coefficient greater than 4.9 (The Petroleum HPV Testing Group, 2002).

### **3.5 Water Solubility**

There is water solubility data available for seven of the eight members of this test plan (Table 1). The petroleum oxidate in subcategory 1 has a water solubility of 59.34 ppm at 25 deg C. The petroleum oxidates and derivatives in subcategory 2 have very low water solubilities that range from 0.35 to 1.29 ppm at 25 deg C. The untested member 68603-12-3, oxidized Me ester Na salt, is expected to have a water solubility similar to 68603-10-1 and 38603-11-2, the oxidized Me ester Ba salt and Ca salt respectively. There is sufficient water solubility data available for the members of this test plan; therefore, additional testing is not required.

**Table 1 Physicochemical Properties**

CAS #	Avg. MW	Melting Point deg C	Boiling Point Range deg F	Vapor Pressure at 25 C	Partition Coefficient	Water Solubility at 25 C
<i>Subcategory 1</i>						
64742-98-9	285	-31.03	196 to 842	69 Pa	Estimated 3.3 – 7.06	59.34 ppm
<i>Subcategory 2</i>						
64743-00-6	744	33.64	393 to >1200	<1Pa	Estimated >4.9	1.25 ppm
64743-01-7	2037	38.93	417 to >1200	<1Pa	Estimated >4.9	3.47 ppm
68425-34-3	2260	49.87	665 to >1200	<1Pa	Estimated >4.9	0.35 ppm
68602-85-7	1294	38.02	400 to >1200	<1Pa	Estimated >4.9	0.54 ppm
68603-10-1	1189	42.86	380 to >1200	<1Pa	Estimated >4.9	0.50 ppm
68603-11-2	ND	41.84	379 to >1200	<1Pa	Estimated >4.9	1.29 ppm
68603-12-3	ND	ND	ND	ND	Estimated >4.9	ND

ND – Not determined.

#### 4.0 Environmental Fate

##### 4.1 Photodegradation

Direct photochemical degradation occurs when a chemical substance absorbs solar radiation. If the amount of absorbed energy is high enough, then the resultant excited state of the chemical may lead to its transformation. Simple chemical structures can be examined to determine whether a chemical has the potential for direct photolysis. First order reaction rates can be calculated for some chemicals that have a potential for direct photolysis using the procedures of Zepp and Cline (1977). Photodegradation of the materials in this test plan cannot be measured directly because of their complex mixture. However, UV light absorption of representative chemicals of each subcategory will be evaluated to identify those that have the potential to degrade in solution. For those that have a potential for direct photolysis in water, first order reaction rates will be calculated. The results will be summarized in a robust summary for this endpoint.

Indirect photodegradation (atmospheric oxidation) occurs because of hydroxyl radical (OH<sup>-</sup>) attack. Atmospheric oxidation can be measured using OECD guideline 113 or estimated using models accepted by the EPA. The computer

program AOPWIN, which is used by OPPTS calculates a chemical half-life based on an overall OH- reaction rate constant, a 12-hr day, and a given OH- concentration. Photodegradation will be calculated for several representative chemical components of each subcategory in this test plan. The resulting calculations will be summarized in a robust summary for this endpoint.

#### **4.2 Hydrolysis**

Hydrolysis of a chemical is a transformation process in which an organic chemical reacts with water, forms a new carbon oxygen bond, and cleaves a carbon-X bond in the original molecule, where X is the leaving group. In order for hydrolysis to occur, the chemical must contain a suitable leaving group. Chemicals that have the potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (Neely, 1985).

The complex mixture and low water solubility of the materials in this test plan limits the ability to estimate or measure hydrolysis rates. However, the materials in this test plan do not contain hydrolyzable functional groups therefore hydrolysis if any is expected to be slow. Based on the information available, the members of this test plan will not undergo significant hydrolysis and no additional testing is required.

#### **4.3 Fugacity**

Fugacity modeling compares the distribution of chemicals between environmental compartments (i.e., air, soil sediment, suspended sediment, water, biota). In the document "Determining the Adequacy of Existing Data" the US EPA acknowledges that it accepts data from the widely used Equilibrium Criterion Model (EQC) (Mackay, 1996). Fugacity modeling will be performed using the EQC model Level III for several representative chemical components of each subcategory in this test plan. The results will be summarized in a robust summary for this endpoint.

#### **4.4 Biodegradation**

The materials of this test plan have not been tested for biodegradation. Three members will be tested using OECD guideline 301F. The oxidized light distillate, 64742-98-9, will be tested for subcategory 1. The oxidized petroleum, 64743-00-6, and the oxidized Me ester Ca salt, 68603-11-2 will be tested for subcategory 2. The data generated on these materials will be extrapolated to the other members of the subcategory. Due to the similarities between the members of this subcategory, extrapolation to the untested members is appropriate.

**Table 2 Environmental Fate**

CAS #	Photodegradation	Hydrolysis	Fugacity	Biodegradation
<i>Subcategory 1</i>				
64742-98-9	ND	Slow	ND	ND
<i>Subcategory 2</i>				
64743-00-6	ND	Slow	ND	ND
64743-01-7	ND	Slow	ND	ND
68425-34-3	ND	Slow	ND	ND
68602-85-7	ND	Slow	ND	ND
68603-10-1	ND	Slow	ND	ND
68603-11-2	ND	Slow	ND	ND
68603-12-3	ND	Slow	ND	ND

ND – Not determined

## 5.0 Ecotoxicology Data

### 5.1 Acute Fish

Acute fish toxicity data is available for one member of subcategory 2 (Table 3). The member tested, 68603-11-2 oxidized methyl ester Ca salt, has a low acute fish toxicity. The test was conducted using rainbow trout following OECD guideline 203. This material has a 96 hr LL50 of 3540 mg/L. Due to the similarities between the members of this subcategory, read across to the untested members is appropriate. Acute fish toxicity data is not available for the member of subcategory 1. The oxidized light distillate, 64742-98-9, will be tested for acute fish toxicity using OECD guideline 203.

### 5.2 Acute Algae

Acute algae toxicity data is available for one member of subcategory 2 (Table 3). The member tested, 68603-11-2 oxidized methyl ester Ca salt, has a low acute algae toxicity. The acute algae toxicity test was conducted using *Selenastrum capricornutum* following OECD guideline 201. This material has a 72hr EL50 of 3860mg/L. Due to the similarities between the members of the subcategory, read across to the untested members is appropriate. Acute algae toxicity data is not available for the member of subcategory 1. The oxidized light distillate, 64742-98-9, will be tested for fish toxicity using OECD guideline 201.

### 5.3 Acute Invertebrate

Acute Daphnia toxicity data is available for one member of subcategory 2 (Table 3). The member tested, 68603-11-2 oxidized methyl ester Ca salt, has a low acute invertebrate toxicity. The acute invertebrate toxicity test was conducted using *Daphnia magna* following OECD guideline 202. This material has a 48hr LL50 of 7070mg/L. Due to the similarities between the members of this subcategory, read across to the untested members is appropriate. Acute invertebrate toxicity data is not available for the member of subcategory 1. The oxidized light

distillate, 64742-98-9, will be tested for fish toxicity using OECD guideline 202. Pending results of the acute toxicity test, a chronic daphnia study may be performed on the oxidized light distillate.

**Table 3 Ecotoxicology**

CAS #	Acute Fish	Acute Algae	Acute Daphnia
<i>Subcategory 1</i>			
64742-98-9	ND	ND	ND
<i>Subcategory 2</i>			
64743-00-6	ND	ND	ND
64743-01-7	ND	ND	ND
68425-34-3	ND	ND	ND
68602-85-7	ND	ND	ND
68603-10-1	ND	ND	ND
68603-11-2	96hr LL50= 3540mg/L	72hr EL50 =3860 mg/L	48hr LL50= 7070mg/L
68603-12-3	ND	ND	ND

ND- Not determined

## 6.0 Mammalian Toxicology Data

### 6.1 Acute Mammalian Toxicity

Acute oral toxicity data is available for four members of subcategory 2 (Table 4 ). The members tested show a low acute oral toxicity with a LD<sub>50</sub> greater than 2000 mg/kg. Due to the similarities between the members of this subcategory, read across to the untested members is appropriate. Acute oral toxicity data is not available for the member of subcategory 1. However, data generated from the proposed repeated-dose toxicity, reproduction-development toxicity test will be sufficient to fill this data gap.

### 6.2 Genetic Toxicity

#### 6.2.1 Bacterial Mutagenicity

There is mutagenicity data available for three members of this test plan (Table 4). One member of subcategory 1 and two members of subcategory 2 were tested using the ASTM E1687-98 test method. This method is not adequate for the purposes of the HPV program. One member from each subcategory will be tested using OECD guideline 471. The oxidized light distillate, 64742-98-9, will be tested for subcategory 1 and the oxidized petroleum, 64743-00-6, will be tested for subcategory 2. This member of subcategory 2 has been chosen for testing due to its increased potential for toxicity based upon its physicochemical properties. This material has the lowest molecular weight indicating it will be more bioavailable than the other members of subcategory 2. This material also has a high water solubility indicating that the material will be more lipophilic, which will

increase its absorption. The results from the bacterial mutagenicity test will be bridged to the other members of the subcategory 2. Due to the similarities between the members of this subcategory, read across to the untested members is appropriate.

### **6.2.2 Chromosomal Aberration**

The materials of this test plan have not been tested for clastogenic activity. One member from each subcategory will be tested using OECD guideline 473. The oxidized light distillate, 64742-98-9, will be tested for subcategory 1 and the oxidized petroleum, 64743-00-6, will be tested for subcategory 2. This member of subcategory 2 has been chosen for testing due to its increased potential for toxicity based upon its physicochemical properties. This material has the lowest molecular weight indicating it will be more bioavailable than the other members of subcategory 2. This material also has a high water solubility indicating that the material will be more lipophilic, which will increase its absorption. The results from the chromosomal aberration test will be bridged to the other members of the subcategory 2. Due to the similarities between the members of this subcategory, read across to the untested members is appropriate.

### **6.3 Repeated Dose Toxicity**

The materials of this test plan have not been tested for chronic toxicity. The member of subcategory 1, 64742-98-9 will be tested using OECD guideline 422. This member has been chosen for testing because it is projected to be the upper boundary of toxicity based upon its physicochemical properties. This material has the lowest molecular weight, which indicates it will be more bioavailable than the other members of the category. This material also has a higher degree of water solubility relative to the other members of the category, which indicates that the material will be more readily bioavailable. Pending the outcome of this study an additional repeated dose toxicity test may be performed on one member of subcategory 2. A tiered testing approach is planned, as an animal sparing technique. The results from the repeated dose toxicity test will be bridged to the other members of the category. Due to the similarities between the members of this category, read across to the untested members is appropriate.

### **6.4 Reproductive and Developmental Toxicity**

The materials of this test plan have not been tested for reproductive or developmental toxicity. The member of subcategory 1, 64742-98-9 will be tested using OECD guideline 422. This member has been chosen for testing because it is projected to be the upper bound of toxicity based upon its physicochemical properties. This material has the lowest molecular weight, which indicates it will be more bioavailable than the other members of category. This material also has a higher degree of water solubility relative to the other members of the category, which indicates that the material will be more readily bioavailable. Pending the outcome of this study an additional reproductive and developmental toxicity test may be performed on one member of subcategory 2. The results from the

reproductive/developmental toxicity test will be bridged to the other members of the category. Due to the similarities between the members of this category, read across to the untested members is appropriate.

**Table 4 Mammalian Toxicology**

CAS #	Acute Health	Bacterial Mutagenicity	Chromosomal Aberration	Repeated dose	Reproductive/ Developmental
<i>Subcategory 1</i>					
64742-98-9	ND	NA	ND	ND	ND
<i>Subcategory 2</i>					
64743-00-6	LD50 >5000mg/kg	NA	ND	ND	ND
64743-01-7	LD50 5000mg/kg	NA	ND	ND	ND
68425-34-3	ND	ND	ND	ND	ND
68602-85-7	ND	ND	ND	ND	ND
68603-10-1	LD50 >2000mg/kg	ND	ND	ND	ND
68603-11-2	LD50 >15mL/kg	ND	ND	ND	ND
68603-12-3	ND	ND	ND	ND	ND

ND – Not Determined

NA – Data available but not adequate for purposes of the HPV Challenge Program

**7.0 Test Plan Summary (Table 5)****7.1 Physical and Chemical Properties**

- The physical and chemical properties for the untested member 68603-12-3, oxidized Me ester Na salt, will be bridged from 68603-10-1, oxidized Me ester Ba salt and 68603-11-2, oxidized Me ester Ca salt. Adequate data is available for all physical and chemical parameters. No additional testing is required.

**7.2 Environmental Fate**

- Photodegradation data will be calculated for representative chemical components for the materials in subcategory 1 and 2.
- Hydrolysis is expected to be slow for the materials in this test plan and no additional testing is required
- Fugacity data will be calculated for representative chemical components for the materials in subcategory 1 and 2.
- Biodegradation data will be measured using OECD guideline 301F for the member of subcategory 1 (64742-98-9) and for (64743-00-6) and (68603-11-2 in subcategory 2. Data generated for the members of subcategory 2 will be bridged to the other members of subcategory 2.

**7.3 Ecotoxicology Data**

- Acute fish toxicity data is not available for the member of subcategory 1. The member of subcategory 1 (64742-98-9) will be tested using OECD guideline 203.
- Acute algae toxicity data is not available for the member of subcategory 1. The member of subcategory 1 (64742-98-9) will be tested using OECD guideline 201.
- Acute invertebrate toxicity data is not available for the member of subcategory 1. The member of subcategory 1 (64742-98-9) will be tested using OECD guideline 202. Pending outcome of the acute test a chronic daphnia test may also be performed.

**7.4 Mammalian Toxicity Data**

- Acute mammalian toxicity data is not available for the member of subcategory 1. Adequate data will be generated during the proposed repeated dose toxicity test with the reproductive and developmental screening test using OECD 422. No additional testing is required.
- Bacterial mutagenicity data is inadequate for the purpose of the HPV Challenge program. The member of subcategory 1 (64742-98-9) and one member of subcategory 2 (64743-00-6) will be tested using OECD guideline 471. Data generated for the member of subcategory 2 will be bridged to the other members of subcategory 2.
- Chromosomal aberration data is not available for the members of this test plan. The member of subcategory 1 (64742-98-9) and one member of subcategory 2 (64743-00-6) will be tested using OECD guideline 473. Data generated for the member of subcategory 2 will be bridged to the other members of subcategory 2.

- Repeated dose toxicity data is not available for the members of this test plan. The member of subcategory 1 (64742-98-9) will be tested using OECD guideline 422. Pending outcome of the test an additional test may be performed on one member of subcategory 2 or data will be bridged to the other members of the category.
- Reproductive and developmental toxicity data is not available for the members of this test plan. The member of subcategory 1 (64742-98-9) will be tested using OECD guideline 422. Pending outcome of the test an additional test may be performed on one member of subcategory 2 or data will be bridged to the other members of the category.

**Table 5 Test Plan Summary**

	64742-98-9	64743-00-6	64743-01-7	68425-34-3	68602-85-7	68603-10-1	68603-11-2	68603-12-3
Melting Point								RA
Boiling Point Range								RA
Vapor Pressure								RA
Partition Coefficient								
Water Solubility								RA
Photodegradation	M	M	RA	RA	M	RA	RA	RA
Hydrolysis								
Fugacity	M	M	RA	RA	M	RA	RA	RA
Biodegradation	T	T	RA	RA	RA	RA	T	RA
Acute Fish	T	RA	RA	RA	RA	RA		RA
Acute Algae	T	RA	RA	RA	RA	RA		RA
Acute Daphnia	T	RA	RA	RA	RA	RA		RA
Acute Health	RA			RA	RA			RA
Bacterial Mutagenicity	T	T	RA	RA	RA	RA	RA	RA
Chromosomal Aberration	T	T	RA	RA	RA	RA	RA	RA
Repeated dose	T	T*/RA	RA	RA	RA	RA	RA	RA
Reproductive/ Developmental	T	T*/RA	RA	RA	RA	RA	RA	RA

T= Test; T\* = Test pending results of proposed testing; RA= Readacross; M= Computer modeling proposed; = adequate data exists

**8.0 References**

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