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12/12/2022

Additional Amendment to PP3439GG_V007 Application

Permit Reference Number:	PP3439GG
Operator:	Fine Organics Limited
Project Reference:	FPM (Workshop 2)

Dear Andy,

Please find following an additional amendment to PP3439GG_V007 Application.

Please do not hesitate to contact me if you require any further information to support this notification.

Yours sincerely,

Gabrielle Hudson
Environmental & Regulatory Compliance Officer

Lianhetech Seal Sands is a trading name of Fine Organics Limited Company registered in England No. 01532065

Permit Reference Number:	PP3439GG
Operator:	Fine Organics Limited
Related permit activity:	Schedule 1 Table S1.1 Section 4.1 Part A (1) (1)
Project Reference:	**FPM** (Workshop **2**)
Date of proposed change:	September 2023

1 Details of Proposed Change

1.1 New Process Introduction

Fluopyram (FPM) is an active fungicide for the American market and has been manufactured at LSS since 2013 across Workshops 2 and 3. The existing process operates in Workshop 2.

The process currently operates with a throughput of 6300 kg/week and due to customer demand will expand with the introduction of an extra stream to a throughput of 8400 kg/week from September 2023 .

The additional stream will process the initial 3 reactions (up to the PyNa step) then will converge into the existing equipment for the decarboxylation step and isolation. The existing assets have been optimised to produce up to 320 tonnes per year. Once the additional stream is incorporated, the process will produce up to 400 tonnes per year.

1.2 Process Description

The process consists of substituting dimethylmalonate onto 2,3-dichloro-5-trifluoropyridine under a vacuum azeotrope to remove water. This is then coupled with 2-trifluoromethyl-acetoxymethyl-benzamide. Following a water wash the intermediate is saponified with sodium hydroxide then decarboxylated with hydrochloric acid. The final product is crystallised from methanol/water then isolated at 15^{o}C by filtration on centrifuge and washed with methanol/water. The product is discharged as a water wet cake (LOD <35%). Solvent is distilled and recycled throughout the process; these include dimethylacetamide, toluene and methyl tert butyl ether (MTBE).

The wet product is then dried in two driers. The drying consists of removal of methanol/water at 70^{o}C maximum contents temperature and a vacuum of <50mbara.

1.3 Equipment

Equipment Description and Duty	MOC	Capacity
Current Assets		
V215 Py-malonester formation	GLMS	9090
V206 Py-malonester formation	GLMS	13635
V207 Py diester formation reaction	GLMS	13635
V220 Py-Na formation reaction	GLMS	9090
V218 Fluopyram formation reaction	GLMS	9090
V261 centrifuge feed vessel	HST	9090
F2-404 - Product Isolation - Heinkel		
V224 - Stirred header for Py-Cl in DMM (to V215)	GLMS	1362
V233 - Stirred header for Py-Cl in DMM (to V218)	GLMS	1362
H222 - 1500 L GLMS Header - HCl addition	GLMS	2270
R2-046 - Circulated receiver Methanol/Water filter wash	GLMS	6820
R227 - DM-Ac distillate for re-use	GLMS	4545

R241 - azeotrope receiver (from V215)	GLMS	2270
R231 - azeotrope receiver (from V206)	GLMS	2270
R225 - Fores receiver (from V207)	GLMS	4545
R226 - MTBE distillate for re-use (from V220)	GLMS	4545
R2-065 - Aqueous separation layer (effluent) ex V207	GLMS	4545
R222 - Mother Liquors and Washes	GLMS	9090
R2-058 - Toluene distillate for re-use (V215)	GLMS	4545
R224 - Toluene distillate for re-use (V206)	GLMS	4545
D203 - Product drier	GLMS	4000
D202 - Product drier	GLMS	3000
Expansion Stream		
V222 Py-malonester formation	HST	9090
V216 Py diester formation reaction	GLMS	9090
V217 Py-Na formation reaction	HST	9090
V225 - Stirred header for Py-Cl in DMM (to V222)	GLMS	1362
R2057 - DM-Ac distillate for re-use (from V216)	GLMS	5000
R2-066 - Toluene distillate for re-use (V222)	GLMS	9090
R228 - azeotrope receiver (from V222))	GLMS	2270
R230 - Fores receiver (from V216)	GLMS	4545
R232 - MTBE distillate for re-use (from V217)	SS	4545
R2-025 - Aqueous separation layer (effluent) ex V216	HST	9090
R233 - Aqueous separation layer (effluent) ex V217	GLMS	4545

1.4 Process Flow Diagram

Process flow diagram provided as Confidential document:
PP3439GG_Fine Organics Limited_PFD_FPM

1.5 Process Outline

Process flow diagram provided as Confidential document:
PP3439GG_Fine Organics Limited_Process Outline_FPM

2 Environmental Impact Assessment

2.1 General Management

The introduction of this change is managed by the Change Management Authorisation Procedure GEN/001.

2.2 Energy Efficiency

Energy efficiency changes are not considered as part of this notification.

2.3 Raw materials

The management of the raw materials is detailed in procedure QA/050.

MATERIALS USED	CLASSIFICATION
N,N-Dimethylacetamide (DMAC)	H312: Harmful in contact with skin. H319: Causes serious eye irritation. H332: Harmful if inhaled. H360D: May damage the unborn child.
Toluene	H225: Highly flammable liquid and vapour. H373: May cause damage to organs through prolonged or repeated exposure. H315: Causes skin irritation. H336: May cause drowsiness or dizziness. H361d: Suspected of damaging the unborn child.
Fluopyram (FPM)	H302: Harmful if swallowed. H371: May cause damage to organs (liver). H411: Toxic to aquatic life with long lasting effects.
Dimethyl malonate (DMM)	H315: Causes skin irritation. H319: Causes serious eye irritation. H335: May cause respiratory irritation.
2,3-Dichloro-5-trifluoromethyl pyridine (PyCl)	H302+332: Harmful if swallowed or if inhaled. H317: May cause an allergic skin reaction. H318: Causes serious eye damage. H412: Harmful to aquatic life with long lasting effects.
TFMB-Acetate in DMAC (50%w/w)	H302: Harmful if swallowed. H315: Causes skin irritation. H317: May cause an allergic skin reaction. H319: Causes serious eye irritation. H360D: May damage the unborn child. H413: May cause long lasting harmful effects to aquatic life.
MTBE	H225: Highly flammable liquid and vapour. H315: Causes skin irritation.
Hydrochloric acid 36%	H314: Causes severe skin burns and eye damage. H335: May cause respiratory irritation

25% Sodium hydroxide	H314: Causes severe skin burns and eye damage.
Methanol	H225: Highly flammable liquid and vapour. H331: Toxic if inhaled. H311: Toxic in contact with skin. H301: Toxic if swallowed. H370: causes damage to organs.
Aluminium nitrate nonahydrate 11% aqueous solution	H315: Causes skin irritation. H319: Causes serious eye irritation. H272: May intensify fire; oxidiser.
Glacial acetic acid	H226: Flammable liquid and vapour. H314: Causes severe skin burns and eye damage.
Potassium Hydroxide Flake	H302: Harmful if swallowed. H314: Causes severe skin burns and eye damage.

2.4 Waste and Emissions to Sewer

All raw material packaging will be containerised and controlled using the waste assessment and coding procedure TF/098. Where it is appropriate recycling, reuse and recovery will be employed.

All effluent waste streams will be controlled using the waste stream assessment and coding procedure TF/098. Where it is appropriate recycling, reuse and recovery will be employed.

The key process streams are:

- Scrubber waste – treatment
- Acidic waste – off site high temperature incineration
- Solvent wastes (MeOH) in small quantities – recovery into SLF.

All off-site transfer of waste will be controlled using procedure TF/100.

There are no process waste transfers to sewer.

2.5 Emissions to Air

The process will vent to the registered air emission point A1/2.

Process off gas

During the 36% Hydrochloric acid charge into V218, decarboxylation takes place evolving carbon dioxide, 4.495kmol.

Off gassing is partially captured by 2 counter current scrubbers containing sodium hydroxide solution. Each of the counter current scrubbers is charged with 300L of 25% NaOH giving a total available of 4.688kmol.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

4.495kmol of CO_2 would require 8.990kmol of NaOH to completely capture the off gas. This however cannot be charged to the scrubbers, as the higher concentration of NaOH would lead to precipitation of Na_2CO_3 leading to blockages. The remaining carbon dioxide, 2.151kmol, therefore passes through another counter current scrubber containing water before venting to air.

The scrubbers are charged with fresh 25% NaOH and water every batch.

VOC

The condenser capabilities are such that vapours from activities in the process vessels and ancillary equipment will be condensed and losses will be minimal. Condenser services will be dowtherm (heat transfer medium). The estimated VOC emissions to air for each unit operation and total batch cycle have been calculated using equipment data and physical properties of Dimethylacetamide (DMAC), Toluene, MTBE, Methanol and Acetic Acid.

Total emission for DMAC is estimated at 3.3kg per batch; this is 0.039kg per hour per batch.
The most significant unit operation/short term activity is the Vacuum Distillation.

Total emission for Toluene is estimated at 22.1kg per batch; this is 0.26kg per hour per batch.
The most significant unit operation/short term activity is the Vacuum Distillation.

Total emission for MTBE is estimated at 74.2kg per batch; this is 0.89kg per hour per batch.
The most significant unit operation/short term activity is the Vacuum Distillation.

Total emission for Methanol is estimated at 64.4kg per batch; this is 0.77kg per hour per batch.
The most significant unit operation/short term activity is the Centrifuge.

Total emission for Acetic Acid is estimated at 0.477kg per batch; this is 0.006kg per hour per batch.
The most significant unit operation/short term activity is the Vacuum Distillation.

Using H1 assessment tool, the estimated process contributions have been calculated as the maximum ground level concentration for DMAC, Toluene, MTBE, Methanol and Acetic Acid. These contributions as a proportion of the EAL (assumed for MTBE) have also been calculated.

The process contribution for DMAC with a defined EAL is below level for significant impact.
The process contribution for Toluene with a defined EAL is below level for significant impact.
The process contribution for MTBE with a modelled EAL is below level for significant impact.
The process contribution for Methanol with a defined EAL is below level for significant impact.
The process contribution for Acetic Acid with a defined EAL is below level for significant impact.

2.6 Air Emissions Risk Assessment

According to the Environment Agency's H1 methodology, it is possible to screen out emissions that result in "insignificant" impacts and those emissions where further assessment is not required, based on the appropriate Environmental Assessment Level (EAL) for each pollutant. Screening of the emissions is achieved using the simplified dispersion factors contained within the H1 methodology. These factors are applied based on the effective stack height of the emission source and are used to estimate the ground level concentration per unit release of pollutant.

The degree of dispersion, and hence the likely ground level concentration, arising from an elevated pollutant release is affected by the presence of other buildings or structures in the vicinity of the stack. These structures can cause downwash to occur, which increases the ground level concentration arising from the emissions and in effect reduces the effective height of the release.

The effective stack height is calculated by assessment of the buildings close to the stack, which could affect the dispersion of the release. An effective stack height has been calculated for the Workshop 2 stack, based on the methodology provided in the EA's H1 Annex F – Air Emissions guidance document. This document states that:

- *"Where the point of discharge is less than 3m above the ground or building on which it is located, or is less than the height of any building within the equivalent of five stack heights,…the effective height of release can be considered to be zero"; and "Where the height of release is greater than 3m above the ground or building on which it is located, but less than 2.5 times the height of the tallest adjacent building, the effective height of release can be estimated:*

$$U_{eff} = 1.66 \times H \{(U_{act} / H) - 1\}$$

Where:

H = height of tallest adjacent building within five stack heights

U_{act} = actual release height

U_{eff} = effective release height."

The Workshop 2 building is the closest tall building to the stack within five stack heights, at 12.8 m at the highest point. The Workshop 2 stack is 17.4m tall and therefore is less than 2.5 times the height of the Workshop 2 building. The effective stack height has therefore been based on the height of the Workshop 2 building as follows.

Effective Height: $1.66 \times 12.8 \{(17.4 / 12.8) - 1\} = 7.6$ m

Using the H1 screening tool, together with the Workshop 2 release conditions, it is possible to estimate the worst-case ground level concentration of pollutant arising from the Workshop 2 source over short term and long-term averaging periods. The predicted process contribution (PC) for each averaging period can then be compared with the pollutant EAL contained in the EPR-H1 guidance, in order to determine the "significance" of the pollutant emission.

The total pollutant emission is defined as having an "insignificant" impact where:

- *Process Contribution (PC) <= 10% of the EAL for short term releases and Process contribution (PC) <= 1% of the EAL for long term releases*

The estimated emissions of DMAC, Toluene, MTBE, Methanol and Acetic Acid from the Workshop 2 stack have been estimated as follows:

Release Rates

Long Term Release Rate = the projected total solvent losses / duration of the batch processing time

Short Term Release Rate = the projected total solvent losses / duration of the key activities

Long Term Effects Release Rate – DMAC:

Total Losses		Batch Processing Time		Release Rate
kg	g	hrs	s	g/s
3.283	3283	120	432000	7.6×10^{-3}

Most Significant Short Term Effects Release Rate – DMAC:

Activity	Losses during Activity		Duration of Activity		Release Rate
	kg	g	hrs	s	g/s
Vac Distillation	3.154	3154	15	54000	5.8×10^{-2}

Long Term Effects Release Rate – Toluene:

Total Losses		Batch Processing Time		Release Rate
kg	g	hrs	s	g/s
22.104	22104	120	432000	5.12×10^{-2}

Most Significant Short Term Effects Release Rate – Toluene:

Activity	Losses during Activity		Duration of Activity		Release Rate
	kg	g	hrs	s	g/s
Vac Distillation	19.653	19653	50	180000	1.09×10^{-1}

Long Term Effects Release Rate – MTBE:

Total Losses		Batch Processing Time		Release Rate
kg	g	hrs	s	g/s
74.168	74168	120	432000	1.72×10^{-1}

Most Significant Short Term Effects Release Rate – MTBE:

Activity	Losses during Activity		Duration of Activity		Release Rate
	kg	g	hrs	s	g/s
Vac Distillation	48.360	48360	10	36000	1.34

Long Term Effects Release Rate – Methanol:

Total Losses		Batch Processing Time		Release Rate
kg	g	hrs	s	g/s
64.408	64408	120	432000	1.49×10^{-1}

Most Significant Short Term Effects Release Rate – Methanol:

Activity	Losses during Activity		Duration of Activity		Release Rate
	kg	g	hrs	s	g/s
Centrifuge	59.592	59592	18	64800	9.2×10^{-1}

Long Term Effects Release Rate – Acetic Acid:

Total Losses		Batch Processing Time		Release Rate
kg	g	hrs	s	g/s
0.477	477	120	432000	1.0×10^{3}

Most Significant Short Term Effects Release Rate – Acetic Acid:

Activity	Losses during Activity		Duration of Activity		Release Rate
	kg	g	hrs	s	g/s
Vac Distillation	0.267	267	15	54000	4.9×10^{-3}

Air Release Point

Description	Location	Activity	Effective Height m	Efflux Velocity m/s	Total Flow m^3/hr
A1/2	Workshop 2	Batch manufacture	7.6	6.6	13620

Environment Assessment Level

Substance	Long Term Effects	Short Term Effects
	EAL µg/m^3	EAL µg/m^3
DMAC	360	7200
Toluene	1910	8000
MTBE	1835*	36700*
Methanol	2660	33300
Acetic Acid	250	3700

*There is no EAL assigned for MTBE
EA guidance advises the use of occupation exposure limits (OEL) to derive long and short term EALs.
OEL's are available from EH40 guidance.
EH40 guidance gives the long-term exposure limit (8-hour TWA reference period) for MTBE as 183.5 mg/m3 and the short-term exposure limit as 367 mg/m3.

	Long Term EAL (as an annual average)	Long Term EL (mg/m3)	Short term EAL (as a 1hr average)	Short Term EL (mg/m3)
OES 8-hour TWA	LT EL/100	1.835	-	-
OES STEL 15-minute average	-	-	STEL/10	36.7

Long term release rate and the greatest contributing short term activity release rate as described above have been entered into the H1 screening tool.

The ground level concentration per unit release of DMAC, Toluene, MTBE, Methanol and Acetic Acid were assessed using H1 methodology in the Environment Agencies risk assessment tool. The results of the H1 impact assessment are shown below.

Substance	Long Term Effect			
	Conc. mg/m^3	PC µg/m^3	%PC of EAL	>1% of EAL
DMAC	2.0	0.455	0.127	**No**
Toluene	13.5	3.07	0.161	**No**
MTBE	45.5	10.3	0.561	**No**
Methanol	39.4	8.92	0.336	**No**
Acetic Acid	0.3	0.0599	0.024	**No**

Substance	Short Term Effect			
	Conc. mg/m^3	PC µg/m^3	%PC of EAL	>10% of EAL
DMAC	15.3	79.9	1.11	**No**
Toluene	17.0	88.4	1.11	**No**
MTBE	354.2	1845	5.03	**No**
Methanol	243.2	1267	3.81	**No**
Acetic Acid	1.3	6.75	0.183	**No**

Conclusion

All process contributions pass the criteria and may be screened from further assessment as the emissions are likely to have an insignificant impact.