

File No: NA/752

October 1999

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

Polymer in E7581

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT**Chemical Name****1. APPLICANT**

Ethyl Asia Pacific Company of 9/20 Berry Street NORTH SYDNEY NSW 2060 has submitted a limited notification statement in support of their application for an assessment certificate for Polymer in E7581.

2. IDENTITY OF THE CHEMICAL

The chemical name, CAS number, molecular and structural formulae, details of the polymer composition and residual monomers, specific functional group identities, details of manufacture and formulation and details of exact import volume have been exempted from publication in the Full Public Report.

Marketing Name: Polymer in E7581

Number-Average

Molecular Weight (NAMW): 1019

Weight-Average 1530

Molecular Weight (WAMW):

Maximum Percentage of Low Molecular Weight Species

Molecular Weight < 500: 6

Molecular Weight < 1 000: 38

Polydispersity (Mw/Mn): Approximately 1.5

Method of Detection and Determination:

No specific methods to determine the structure and quantitation of the polymer. The structure is deduced from chemistry knowledge and the structure of the precursors.

Spectral Data:

A GPC (Gel Permeation Chromatography) trace and printout was supplied to determine the NAMW and percentage of low molecular species.

An Infra Red (IR) spectra for the mixture was supplied as the notified polymer is prepared in solvent and is never isolated.

Comments on Chemical Identity

A GPC trace and printout was supplied for the intermediate polymeric derivative to estimate the NAMW and percentage of low molecular species of the notified polymer. The notifier indicates that the GPC trace of the notified polymer goes from an initial somewhat Gaussian shape to a distorted unsymmetrical shape with a very long tail. This tailing produces inaccurate results, which incorrectly portrays these types of polymers as having inordinate amounts of low molecular weight species. The notifier indicates that this difficulty with GPC data on these polymers is the result of an absorption phenomenon. The head group on the notified polymer is very polar and causes it to stick to the gels and resins used in the GPC column resulting in tailing.

The estimates of the NAMW and percentage of low molecular species of the notified polymer come from adding the molecular weight values of the polymeric intermediates and the mass units of a chemical substance that, when reacted together, form the notified polymer.

An IR chromatograph was also submitted for identification of the notified substance.

3. PHYSICAL AND CHEMICAL PROPERTIES

Unless otherwise indicated, the data below represents that of the notified polymer in petroleum solvent naphtha.

Appearance at 20°C and 101.3 kPa:	Amber viscous liquid
Boiling Point:	Not determined (see comments below)
Density:	0.908 g/cm ³ at 15.6 °C
Particle Size:	Not applicable
Vapour Pressure:	Not determined; expected to be low
Water Solubility:	< 10.0 mg/L (see comments below)
Partition Co-efficient (n-octanol/water):	Not determined
Hydrolysis as a Function of pH:	Not determined
Adsorption/Desorption:	Not determined
Dissociation Constant:	Not determined
Flash Point:	41°C (Closed Cup)
Autoignition Temperature:	Not determined

Explosive Properties:	None
Flammability Limits:	Combustible as formulated. Oxides of carbon, hydrogen and nitrogen are produced.
Reactivity/Stability:	Stable under normal conditions
Kinematic Viscosity	193 x 10 ⁻⁶ m ² /s at 40 °C (target); 20 x 10 ⁻⁶ m ² /s at 100 °C (typical).
Loss of monomers, additives, impurities:	None expected

Comments on Physico-Chemical Properties

The notified polymer is prepared in solvent and never isolated as a defined entity.

The boiling point of the notified chemical was not determined. The notifier estimates that the polymer will have a low vapour pressure due to its high molecular weight.

The water solubility of the notified chemical was determined at pH 6.3 by the OECD TG 105 HPLC method to be << 10 mg/L, which is below the detection limit.

The notified polymer contains no functional groups that are expected to hydrolyse in the environmental pH range of 4 to 9.

The partition coefficient and adsorption/desorption of the notified polymer were not determined. The notified polymer is expected to be insoluble in water and will largely partition into n-octanol rather than water. Due to its low water solubility and surface activity, the polymer is expected to become associated with the organic component of soils and sediments.

No dissociation constant data were provided. The polymer has secondary and tertiary amine groups that may be protonated at low pH and lead to increased water solubility. However, in view of the very large non-polar groups, the extent of this is unclear.

The polymer is not a dangerous good (Federal Office of Road Safety, 1992). The classification of the fuel additive package in which the polymer will be contained is a Class 3 Flammable Liquid, Packing Group III.

4. PURITY OF THE CHEMICAL

Degree of Purity:	Very high
Maximum Content of Hazardous Residual Monomers:	No hazardous residual monomers are present in the polymer.

Additives/Adjuvants: Petroleum solvent naphtha; not classifiable as a hazardous substance in terms of benzene or PNA content or measured kinematic viscosity.

5. USE, VOLUME AND FORMULATION

The polymer is intended for use as a detergent additive in unleaded petrol. The notifier claims that the detergent additive in conjunction with a polymeric carrier will serve to reduce the formation of deposits in carburettors, fuel injectors and intake valves as well as reduce combustion chamber deposits in petrol engines.

The notified polymer will not be manufactured in Australia but will be imported as a component in fuel additive packages at less than 50% w/w. The estimated import volume of the notified polymer in the fifth year is less than 300 tonnes. Of this amount approximately 80% will be imported in ISO containers and approximately 20% in drums. These containers will go to customer refineries directly after importation.

At the refinery/terminal facility the petrol additive is typically blended with petrol immediately just prior to transport of the fuel to the petrol station. The additive package is injected automatically as the fuel is pumped into the delivery tanker. The additive is injected into unleaded petrol on a volumetric basis that will result in less than 0.1% w/w notified polymer in the final fuel.

A maximum of 1500 service stations is expected to store fuel containing the notified chemical.

6. OCCUPATIONAL EXPOSURE

Number and Category of Workers

Import and Transportation: 20 workers;

Storage Facility: 24 plant operators and maintenance workers;

Refinery/Terminal Facility: 100 plant operators and maintenance workers.

Dockside and Transport

The notified polymer will be imported in drums or ISO containers. Occupational exposure is not expected except in the event of a spill. No repackaging of drums or ISO containers is required as these are delivered directly to the customer site.

Refinery/Terminal Facility

Exposure may occur during addition of the additive package to the fuel due to the use of automated processes and dedicated delivery lines and equipment. However, it is expected to be confined to skin contamination with drips and spills during the connection and disconnection of transfer lines and equipment. Chemical goggles and chemical resistant gloves are recommended by the notifier for workers when handling the additive package. Engineering controls in the form of automated delivery systems already in place at the refineries will minimise the potential for exposure during blending.

Service Stations

Exposure to very low concentrations of the notified polymer in the final fuel by mechanics and service station personnel may occur.

Worker Education and Training

The notifier states that the additive product containing the notified polymer will be handled by trained workers knowledgeable of safe handling procedures for fuels and fuel additives.

7. PUBLIC EXPOSURE

The notified polymer will be used as a minor component in petrol. Hence, direct contact with the notified polymer by members of the public is unlikely.

8. ENVIRONMENTAL EXPOSURE

Release

The polymer will be transported via road in closed containers. Potential release would only be through accidental spills. The Material Safety Data Sheet (MSDS) details procedures to protect the environment in these cases. Once received by the customers, the fuel additive package containing the polymer will be blended into the petrol at < 0.1% w/w at their facilities. This is an automatic process using dedicated delivery lines and equipment and the notifier claims that no measurable amount of the notified chemical is expected to be lost due to spills during this formulation process.

The ISO containers used to transport and store the fuel additive will be continually reused without rinsing. The notifier estimates that a maximum of 4% of the fuel additive package will remain as residues in empty drums. This corresponds to < 5kg of notified polymer in each 200 L drum. At a maximum import volume of < 60 tonnes of notified polymer in drums, < 1 tonne of notified polymer waste will be generated per year. The notifier indicates that the empty drums and their residues will be sent to a certified drum recycler where they will be rinsed and the rinsate disposed in accordance with government regulations.

The notifier expects that a maximum of 1500 service stations may store fuel containing the notified polymer. The probable number of spills for 1500 service stations would be 4.05 per year. If each spill was 200 L, this would result in a total of < 5kg of the notified polymer being lost. These figures given by the notifier are said to be based on a research project carried out at the University of British Columbia, Canada, which investigated the incidents of petrol spills at service stations in the Greater Vancouver region. These figures do not take into account frequent minor spills (< 1 L) that would occur at petrol bowsers as customers fill their vehicles with fuel. Given the low percentage in fuel, the amount of notified polymer lost in these spills would be expected to be very low.

The polymer and additive package will not be directly marketed to the public, but preblended into the petrol sold at service stations.

Fate

Polymer released to soil in either a spill or leak from a storage tank is expected to bind strongly to soil due to its low water solubility. Polymer released to an aquatic environment would tend to partition out of water and into sediment. Once adsorbed to soil/sediment, the fate of the polymer is unknown. The polymer is not expected to cross biological membranes due to the low solubility and high molecular weight, and should not bioaccumulate (Connell, 1989).

Less than 1 tonne of notified polymer waste from drum recycling is expected to enter an aqueous treatment plant. It is anticipated that the notified polymer waste will be part of the solid wastes from the plant and consigned to landfill.

The notifier has indicated that tail pipe emission data on the notified polymer are unavailable. However, the notifier supplied data on an analogue. The only structural difference between the notified polymer and the analogue is the absence of an alkyl group. The data supplied was for a fuel additive package that also contains the carrier fluid E7578, notified and assessed by NICNAS as PLC/120.

Test results provided show no statistical difference in HC, CO and NO_x emissions between test fuel with and without the additive. The long term effect of using detergent fuel additives is to reduce the formation of engine deposits ie “keep clean”, and “clean up” existing engine deposits leading to reduced levels of tail pipe emissions. The analogue in conjunction with its polymeric carrier have been shown to reduce port fuel injector plugging after ~ 500 miles to less than 5% from levels as high as 25%.

The analogue is listed on the US TSCA inventory and, in combination with certain carrier/dispersant additives, is said to be registered for use with US EPA and the California Air Resources Board as a fuel additive.

The notified polymer will need to be tested to ensure that it will meet the upcoming criteria in the Australian Standard, Evaluation of Devices and Additives which Claim to Improve Vehicle Performance (to be AS 4430.2).

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicology data were provided for the notified substance. Summary data on a similar polymeric substance were provided in the submission and are summarised below. The notifier states that the analogue is similar to the notified polymer with respect to its chemical composition and molecular weight distribution.

The test material for each of following tests contains 40% of the substance in process oil. The process oil is the same as that will be used in the manufacture of additive packages containing the notified polymer.

9.1 Acute Toxicity

An acute oral toxicity value of LD₅₀ > 5000 mg/kg in rats was provided indicating that the substance was of very low acute oral toxicity.

9.2 Repeated Dose Toxicity (David, 1990)

<i>Species/strain:</i>	Sprague-Dawley rats
<i>Method of administration:</i>	Oral (gavage)
<i>Dose/Study duration:</i>	0, 325, 625 and 1250 mg/kg for 28 consecutive days; corn oil vehicle
<i>Test method:</i>	OECD TG 407

Clinical observations:

No changes in body weight, weight gains and food consumption were observed for all groups.

Clinical chemistry/Haematology

No toxicologically significant changes were noted.

Pathology:

Significant dose-related increases in absolute and relative liver weights in both sexes were observed but no microscopic changes were noted in the top dose rats.

Result:

The no observed adverse effect level (NOAEL) of the substance was stated to be 1250 mg/kg/d based on the absence of systemic toxicity or pathological effects at this level.

9.3 Genotoxicity

9.3.1 *Salmonella*/Mammalian Microsome Plate Incorporation Mutagenicity Assay (Ames Test) (San and Kruel, 1989)

<i>Strains:</i>	TA 98, TA100, TA1535, TA537 and TA1538
<i>Concentration range:</i>	Without S-9 mix: 0, 100, 333, 667, 222, 6667 µg/plate; With S-9 mix: 0, 100, 333, 1000, 3330, 10000 µg/plate.
<i>Metabolic activation:</i>	Microsomal enzymes derived from Aroclor 1254 induced rat liver (S-9 mix)
<i>Test method:</i>	OECD TG 471 – plate incorporation method
<i>Comment:</i>	No positive response with any of the tester strains was noted either in the presence or absence of metabolic activation.
<i>Result:</i>	The test substance did not induce mutation in the bacterial strains tested.

9.3.2 Micronucleus Assay in the Bone Marrow Cells of the Mouse (Putman and Melhorn, 1989)

<i>Species/strain:</i>	ICR mice
<i>Doses:</i>	0, 363, 1815, 3630 mg/kg
<i>Method of administration:</i>	Single intraperitoneal injection
<i>Test method:</i>	OECD TG 474
<i>Comment:</i>	The ratio of polychromatic erythrocytes to total erythrocytes was not changed in treated mice of both sexes, indicating that the substance did not induce bone marrow toxicity. A statistically significant increase in micronucleated polychromatic erythrocytes was noted at the 72 hours point in male mice at the low dose only, but was considered to be related to the low background rate in the control group at this time point rather than a real increase in the treated group. When compared to the vehicle controls at 24 or 48 hours, no statistically significant increases were noted. No changes were observed at 24 and 48 hours at all doses.
<i>Result:</i>	This test substance did not show evidence of genotoxic activity <i>in vivo</i> in the mouse micronucleus assay.

9.4 Overall Assessment of Toxicological Data

Summary data on a similar polymeric substance were provided. It has very low acute oral toxicity in rats ($LD_{50} > 5000$ mg/kg). The only sign of toxicity in a 4-week oral study was a significant increase in liver weight at 625 and 1250 mg/kg in both sexes, but no correlated microscopic lesions were observed. The NOAEL is 1250 mg/kg/d based on the absence of systemic toxicity or pathological effects at this level. The Ames test and mouse micronucleus assay revealed no indication of genotoxicity both *in vitro* or *in vivo*.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicology data were provided.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The intended use pattern of the polymer in the fuel additive is not expected to result in a significant release to the environment as it is claimed that the polymer is completely destroyed by combustion within the petrol engine, producing oxides of carbon and hydrogen. There are no direct data to support the claim of complete combustion of the polymer to oxides of carbon and hydrogen when the fuel is burnt within the combustion chamber of

petrol engines. However, it is evident that the polymer which is made up of hydrocarbon, nitrogen and oxygen, the normal constituents of petrol, will not survive the temperatures at which the fuel is exploded within the internal combustion engine. The analogue data indicates that the notified polymer will not increase tailpipe emissions.

In the event of spills, the MSDS of the additive package containing the polymer contains information on procedures to enable clean up operators to reduce release to the environment. Minor spills and leaks of the polymer may occur during customer fill ups at petrol service stations. However, given its low percentage in fuel, the loss of the notified polymer in these spills would be expected to be low.

Less than 1 tonne of notified polymer waste from drum recycling is expected to enter an aqueous treatment plant, where it is anticipated that the notified polymer waste will be part of the solid wastes from the plant that will be consigned to landfill. The polymer is unlikely to be mobile given the very low water solubility and high binding affinity to soil. The polymer's large molecular size and very low water solubility should prevent bioaccumulation.

Given the above, environmental exposure and the overall environmental hazard is expected to be low.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

No toxicological data is provided for the notified polymer. Data on a similar polymeric substance were provided in summary form. From the summary data provided, the analogue had low acute toxicity and did not indicate genotoxicity in *in vitro* and *in vivo* assays. A NOAEL of 1250 mg/kg/d was established in a 28-day oral study where increased liver weights were observed. From the limited data available, no hazard classification can be conducted in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (National Occupational Health and Safety Commission, 1999a).

The MSDS indicates that the additive package containing the notified polymer is not classified as hazardous and the product is not expected to irritate the skin or eye. However, respiratory irritation may occur following inhalation of mists or vapours at elevated temperatures. The additive package is not an aspiration hazard. Solvent naphtha (petroleum), an ingredient of the additive package, is listed on the NOHSC *List of Designated Hazardous Substances* (National Occupational Health and Safety Commission, 1999b) but does not meet the kinematic viscosity criteria for classification as an aspiration hazard.

Occupational Health and Safety

During import and transport of the notified polymer, there is unlikely to be any worker exposure, except in the event of a spill. Exposure after a spill would be controlled by use of the recommended practices for spillage clean up given in the MSDS supplied by the notifier.

At refineries and terminals, the handling of fuels and fuel products in general may cause a transitory irritation if adequate precautions are not taken. However, workers at these sites are required to wear personal protective equipment to control exposure. Moreover, the use of dedicated and automatic transfer lines and enclosed, automated injection into fuel will reduce the likelihood of exposure to the additive package. Therefore, no significant health risk is expected for these workers.

Service station workers and mechanics will receive negligible exposure because of the very low concentration (less than 0.1% w/w) of polymer present in the final fuel. Therefore, the risk of adverse health effects arising from exposure to the notified polymer is negligible.

Public Health

Based on the negligible potential for public exposure to the notified polymer arising from its intended use, it is considered that the notified polymer will not pose a significant hazard to public health when used in the proposed manner.

13. RECOMMENDATIONS

To minimise occupational exposure to Polymer in E7581 the following guidelines and precautions should be observed:

- Personal protective equipment should be used in accordance with Australian Standards, namely, AS 1336 and 1337 (safety goggles) (Standards Australia 1994, Standards Australia/Standards New Zealand 1992); AS 2919 and AS 3765.1 (industrial clothing) (Standards Australia 1987, Standards Australia 1990); AS 2161.2 (gloves) (Standards Australia/Standards New Zealand 1998); AS/NZS 2210 (footwear) (Standards Australia/Standards New Zealand 1994).
- Spillage of the notified chemical should be avoided. Spillage should be cleaned up promptly with absorbents which should then be put into containers for disposal;
- Good personal hygiene should be practiced to minimise the potential for ingestion; and
- A copy of the MSDS should be easily accessible to employees.

The notified polymer will need to be tested to ensure that it will meet the upcoming criteria in the Australian Standard, *Evaluation of Devices and Additives which Claim to Improve Vehicle Performance*, to be AS 4430.2 (Standards Australia, 1998).

If the conditions of use are varied from the notified use, greater exposure of the public to the product may occur. In such circumstances, further information may be required to assess the hazards to public health.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the E7581 additive package containing the notified polymer was provided in a format consistent with the requirements of the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (National Occupational Health and Safety Commission, 1994).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the

responsibility of the applicant.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act, secondary notification of the notified chemical shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

16. REFERENCES

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