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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

SUPERFLOC HX Series Flocculant

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Director

Chemicals Notification and Assessment

FULL PUBLIC REPORT

SUPERFLOC HX Series Flocculant

1. APPLICANT

Cyanamid Australia Pty Ltd, 5 Gibbon Road, Baulkham Hills, N.S.W 2153.

2. <u>IDENTITY OF THE CHEMICAL</u>

Based on the nature of the chemical and the data provided, SUPERFLOC HX Series Flocculant, is considered to be non-hazardous. Therefore, the chemical name, other names, CAS number, molecular formula, structural formula, molecular weight and spectral data have been exempted from publication in the Full Public Report and the Summary Report.

Trade names: SUPERFLOC HX-400 Flocculant (Reagent S-7272),

SUPERFLOC HX-100 Flocculant (Reagent S-7012), SUPERFLOC HX-200 Flocculant, SUPERFLOC HX-300 Flocculant, Reagent S-7027, Reagent S-7028,

Reagent S-7256

Maximum percentage of low molecular weight species

(molecular weight < 1000): None known to exist</pre>

3. PHYSICAL AND CHEMICAL PROPERTIES

The notified polymer is produced in a water-in-oil emulsion and never exists in its pure form. The following data relate to the emulsion SUPERFLOC HX-400 (S-7272).

Appearance at 20°C and 101.3 kPa: white to pale yellow liquid

Odour: strong ammoniacal

Melting Point/Boiling Point: not determined, however

expected to be similar to

water

Specific Gravity/Density: approximately 1000 kg/m³ for

the emulsion and 1590 kg/m 3 for the polymer itself {for

density}

Vapour Pressure: not determined, however

expected to be similar to

water

Water Solubility: miscible in water in all

proportions

Hydrolysis: hydrolysis of the polymer

substituents to carboxylates is likely to occur under the alkaline conditions prevailing

on the mud flats

Adsorption/Desorption: polymer is strongly adsorbed

onto mineral surfaces and inorganic particulates

Flash Point: >93.3°C

Flammability Limits: the emulsion is not flammable

Degradation Products: degradation is slow at ambient

temperature and results in low

molecular weight polymer

species

Combustion Products: carbon monoxide, carbon

dioxide, and/or oxides of

nitrogen and sulphur

Autoignition Temperature: the emulsion is not expected

to self ignite

Explosive Properties: the emulsion is not expected

to self ignite as a result of

heat, shock or friction

Reactivity/Stability: no incompatible materials or

unstable conditions are known

No data were provided for partition co-efficient, hydrolysis as a function of pH and dissociation constant. This is acceptable as the measurement of these properties would be difficult and the polymer is likely to be immobile in soil.

The failure to provide data for vapour pressure, partition coefficient and dissociation constant is acceptable given that the polymer is part of a water-in-oil emulsion and any physicochemical data generated would be consistent with the presence of water in the polymer product.

4. PURITY OF THE CHEMICAL

Degree of purity(of the notified chemical alone): approximately 84%

Toxic or hazardous impurities:

(a) Chemical name: sodium hydroxide

Synonyms: caustic soda; lye; soda lye; sodium

hydrate; caustic flake; liquid caustic

CAS No.: 1310-73-2

Weight percentage: 15.0

Toxic properties: mutagen; skin, eye, nose and

respiratory tract irritant;

LD50 (intra-peritoneal, mouse): 40mg/kg (1),

WSA exposure standard: TWA $2mg/m^3$ (2)

(b) Chemical name: 2-propenamide

> acrylamide; acrylic amide; Synonyms:

> > ethylenecarboxamide; propenamide;

vinyl amide

CAS No.: 79-06-1 Weight percentage: <0.007

Toxic properties: mutagen; skin and eye irritant;

experimental carcinogen and neoplastogen; experimental

reproductive effects; LD50 (oral, rat): 170mg/kg (3)

WSA exposure standard: TWA 0.03 mg/m^3 (2)

(c) Chemical name: hydroxylamine

> oxammonium Synonym: CAS No.: 7803-49-8

0.7 Weight percentage:

mutagen; corrosive irritant to the Toxic properties:

> eye, skin and mucous membranes; LD50 (intra-peritoneal, rat): 59mg/kg; LD₅₀ (sub-cutaneous, rat): 29mg/kg; (3)

Non-hazardous impurity (>1% w/w):

Maximum content of residual monomer(s): 15.71

Additives/Adjuvants:

The proportions listed below relate to SUPERFLOC HX-400, SUPERFLOC HX-300 and SUPERFLOC HX-200.

Chemical name	CAS No.	Weight percentage
Notified polymer		10-<30
Ammonia	7664-41-7	<10
Sodium hydroxide	1310-73-2	<10
Surfactants	_	<10
Distillates (petroleum),	64742-47-8	10-<30
hydrotreated light		
Water	7732-18-5	to 100

5. <u>INDUSTRIAL USE</u>

The notified polymer in a water-in-oil emulsion will be manufactured initially in two different formulations, SUPERFLOC HX-400, SUPERFLOC HX-300 and SUPERFLOC HX-200. The flocculant will be used as a settling agent in the process of producing alumina and is expected to give improved tailing separation during bauxite processing. This polymer is currently undergoing product development in the United States.

6. OCCUPATIONAL EXPOSURE

The polymer emulsion will be manufactured at DYNO Industries, Dardanup, WA. It will be produced in a closed vessel on a batch basis and discharged to a bulk tanker (capacity 27000 L) via an automatic valve. Up to 3 kg of ammonia per every batch will be released from the closed reaction vessel. Minimal exposure to ammonia is expected as the vessel will be vented outside the building above the roof line and only 15 kg of polymer (approximately) will remain in the reaction vessel at the end of each batch. Worker contact with the chemical will be limited to cleaning operations at the end of the batch cycles and will involve 8 workers, 1/2 hour per day, 3 days per week. Two additional workers will be involved in the disposal of spoilt material during the manufacturing process.

Approximately 2 bulk tankers per month will be transported by road to the user, where the contents of the bulk tankers will be discharged to bulk storage tanks. From the storage tanks an automatic measuring system will be employed to feed the emulsion directly into the process stream. The notifier states that no direct worker exposure will be associated with these operations.

In the alumina refinery system the emulsion is diluted to 0.0005% w/w. After treatment with the flocculant, sand and mud are washed and transferred to tailings dams. As the majority of the emulsion is tied up with the mud and any free emulsion is diluted further, the notified chemical is not expected to pose a significant health concern to workers at the user's site.

7. PUBLIC EXPOSURE

Public exposure could feasibly occur around the manufacturing site, at an accident during transport to the site of use, from

accidental release at the user's site (including release from tailings dams), and at landfill sites (if product is dumped after cleanup of an accidental factory or roadside spill).

Under correct handling procedures, the potential for public exposure around the manufacturing site (DYNO Industries, Dardanup, WA) is claimed to be minimal. The emulsion will be produced in a closed vessel and discharged via an automatic valve to a bulk tanker. Disposal quantities will be minimal and should be restricted to material spoilt during the manufacturing process, or spillage.

At the user's site, the emulsion will be dosed into the ore treatment system at a concentration of approx. 0.0005% w/w active in the system; no reaction occurs and the emulsion constituents end up in the user's tailings dam.

Transport of the emulsion (classified as a caustic alkali liquid, containing NaOH and ammonia) will take place in 27,000 L bulk road tankers. In accidental spills, disposal of the slippery emulsion can be affected by spreading sand on the material and shovelling it into open drums for subsequent disposal at landfill sites.

8. <u>ENVIRONMENTAL EXPOSURE</u>

As a result of each batch of polymer emulsion manufacture, an estimated 15 kg of polymer will remain in the reaction vessel and 3 kg of ammonia will be released and trapped in acidic scrubbers. Each 15 kg batch of waste polymer is treated by boiling in 3 tonnes of 20% caustic solution followed by dilution in 17 kL of water. The estimated 20 kL of treated waste is transferred to a bulk road tanker for disposal at mud separation dams at the user's site (see below).

Any spilled product as a result of manufacture or transfer to tankers can be contained by adsorption to sand with subsequent disposal in open head drums.

During bauxite processing, the alumina containing liquor is separated from the mud and sand. Approximately 5000 tonnes of caustic red mud and sand are produced daily, which require the use of the flocculant properties of the polymer emulsion to "settle-out" the mud and decant and recycle the water. To handle the vast quantities of red mud and manufacturing wastes, two

large on-site tailing dams have been constructed with a multilayered base of compacted clay and PVC membrane with a further inner layer of yellow sand housing the underdrain system which collects the water. This multilayered base prevents leaching of the dilute caustic liquor containing the notified substance into groundwater, which is very close to the surface in this area.

The caustic sand and mud waste are sent to the first disposal dam for treatment to separate the solids and recycle the water for further use. Superfloc HX-400 is added to this dam. After thickening, the mud slurry is pumped to drying beds, distributed over the surface to a depth of less than one metre and sun dried to at least 65 to 70% solids before distribution of the next mud layer. The remaining supernatant in the settling dam is sent to a second dam where it is returned to the bauxite refinery to be used as wash water to the mud washers, as hose water and as cooling water.

. Fate

The notifier states that the polymer is very stable under a wide range of conditions, but that hydrolysis products will result at the high pH prevailing on the mud flats. Polymeric breakdown products will remain associated with the dried mud, and are therefore likely to accumulate on the mud flats. In the event of torrential rain and subsequent soil erosion the notified polymer may be transported to the aquatic compartment (see below). However, it is likely to remain adsorbed on mud particles, because of its high molecular weight.

The polymer will form water vapour and oxides of carbon and nitrogen on combustion.

9. EVALUATION OF TOXICOLOGICAL DATA

Although not required for the notification of polymers of molecular weight > 1000, toxicity data were included in this submission. Acute toxicity studies were conducted using the emulsion SUPERFLOC HX-100 in accordance with OECD guidelines. The composition of SUPERFLOC HX-100 was stated to be: water (88.3%); notified polymer (5.2%); hydrocarbon oil (4.0%); sodium sulphate (0.8%); ammonia (0.8%); sodium hydroxide (0.5%); hydroxylamine (0.1%); and surfactant (0.3%).

9.1 Acute Toxicity

Table 1 Summary of the acute toxicity of SUPERFLOC HX-100

Test	Species	Outcome	Reference
Oral	Rat	LD ₅₀ : >5000 mg/kg	4
Dermal	Rabbit	LD50: >2000 mg/kg	4
Skin	Rabbit	moderate to severe	4
irritation			
Eye	Rabbit	moderate to severe	4
irritation			
Skin	Mouse	non-sensitising	4
sensitisation			

9.1.1 Oral Toxicity (4)

This study was conducted according to OECD Guideline 401 (5).

One group of ten (5/sex) adult Sprague-Dawley rats were fasted for 18 hours and then administered with the test chemical. A 25% (w/w) aqueous solution was administered at a dose of mg/kg body weight by gavage and the rats were observed for a period of 15 days for clinical signs of mortality. On day 15 all surviving rats were sacrificed by CO₂ exposure and subjected to gross necropsy. No mortality was produced at the treatment dose. Significant clinical signs observed in the males were primarily on days 1 and 2, and included decreased activity, labored breathing and unsteady gait. No significant clinical signs were observed in the females. The mean body weight increased throughout the study for both sexes. No significant gross lesions or abnormalities were noted during terminal gross necropsy.

Results of this study indicate an acute oral LD $_{50}$ of > 5000 mg/kg in rats of both sexes for SUPERFLOC HX-100.

9.1.2 Dermal Toxicity (4)

This study was conducted according to OECD Guideline 402 (6).

The fur from the trunk of ten (5/sex) adult, New Zealand white rabbits was shaved so that no less than 10% of the dorsal body surface area was available for the application of test material. After 24 hours, neat SUPERFLOC HX-100 at a dose of 2000 mg/kg, was spread evenly over the treatment area and the animals were wrapped with occlusive binder to retard evaporation. hours later, the wrappings were removed and the test site wiped to remove remaining material. The rabbits were observed for a period of 15 days for clinical signs of mortality. On day 15, they were sacrificed by an injection of sodium pentobarbital and gross necropsy was performed. No mortality or significant clinical signs were produced and no gross lesion or abnormalities were observed during terminal necropsy at the treatment dose. However, severe dermal irritation characterised by erythema, oedema, bleached skin and eschar formation was noted as well as a decrease in body weight of both sexes.

The results of this study indicate an acute dermal LD $_{50}$ of > 2000 mg/kg in rats of both sexes for SUPERFLOC HX-100.

9.1.3 Inhalation Toxicity

The notifier was unable to provide a study detailing acute inhalational toxicity, however, based on an evaluation of the components of the product and past experience with similar products, the 4h LD $_{50}$ (rat) was estimated to be greater than 2500 ppm.

9.1.4 Skin Irritation (4)

This study was conducted according to OECD Guideline 404 (7).

The fur from the back of three (2 male, 1 female) adult, New Zealand white rabbits was clipped and abraded by incision of the stratum corneum. Twenty-four hours later 0.5 ml neat SUPERFLOC HX-100 was applied occlusively to one intact and one abraded site on each animal. After an exposure period of 4 hours, the wrappings were removed and the test site wiped to remove remaining material. The test sites were evaluated by the Draize method for up to 21 days. Well-defined to severe erythema with

slight to severe oedema was noted for 4 days on both abraded and intact sites. By day 4, eschar formation was noted on one animal and by day 7 all animals exhibited bleached and thickened skin. By day 21 one animal showed very slight to slight erythema with thickened skin and the other two showed no signs of dermal irritation.

The results of this study suggest that SUPERFLOC HX-100 is a moderate to severe skin irritant.

9.1.5 Eye Irritation (4)

This study was conducted according to OECD Guideline 405 (8).

Neat SUPERFLOC HX-100, 0.1 ml, was applied to the right eye of 6 (5 female, 1 male) adult New Zealand white Rabbits. The left eye remained untreated and served as a control. The treated eyes of 3 animals were flushed with physiological saline 30 seconds after application while the others remained unwashed. The eyes were examined for up to 7 days and ocular effects were scored and recorded by the Draize method. In the unwashed group, one animal showed signs of corneal opacity at 24 hour, the two other animals exhibited iritis and conjunctival irritation, with one of these exhibiting blistering of the conjuctiva at 1 hour, and one showed no signs of irritation during the study. By day 7 no occular irritation was present in this group. In the washed group, corneal opacity was observed at 24 hour in one animal. 2 rabbits exhibited conjunctival erythema and chemosis, with one of these showing blistering of the conjunctiva at 1 hour. Ocular irritation had subsided at 48 hours in 2 of these animals and by 7 days in the remaining rabbit.

The results of this study suggest that SUPERFLOC HX-100 is a moderate to severe eye irritant in rabbits.

9.1.6 Skin Sensitisation (4)

This study was conducted essentially as described by $Gad\ et\ al.$ (9).

Eight adult, female ICR mice were used in a range-finding study to select a maximum, non-corrosive concentration for the induction applications and a maximum non-irritating concentration for the challenge applications. An induction concentration of 25% and challenge concentration of 10% was selected after the

topical applications of various concentrations of SUPERFLOC HX-100 in water to both the clipped abdomen and left ear of the Topical applications were 0.1 ml of 25, 10, 1 and 0.1% (w/v) in water on days 0, 2, and 4 (ear applications were made on day 0 only). Two mice were used per concentration. The definitive study utilised 20 female ICR mice: 10 test, 5 positive control and 5 irritation control. On days 0, 2 and 4, test material (0.1 ml of a 25% w/v solution) was topically applied to the clipped abdomens of the test mice with an intradermal injection of 50% Freund's Complete Adjuvant (0.01-1.05 ml) on both sides of the abdomen on day 0 accompanied the topical application. Irritation control animals were treated with water and positive control animals with dinitrochlorobenzene (DCNB; 0.5% w/v for both induction and challenge). On day 11, test and control animals were challenged by applying test material (0.01 ml of a 10% solution) to both the dorsal and ventral surfaces of the right right ear and appropriate vehicle to the left ear. Twenty-four and 48 hours after challenge animals were anesthetised and the left and right ear thicknesses were measured using a Peacock thickness gauge. Sixty and 100% of DCNB-treated animals showed a positive sensitization response at both 24 and 48 hours respectively. Results of both test and irritation control animals were negative.

The results of this study suggest that SUPERFLOC HX-100 is non-sensitising to the skin.

9.2 Repeated Dose Toxicity (Ref No:)

9.2.1 Genotoxicity: Salmonella typhimurium Reverse Mutation Assay (4)

This study was conducted according to OECD Guideline 471 (10).

SUPERFLOC HX-100 at concentrations of 0, 667, 1000, 3333, 6667 and 10000 µg/plate was tested for gene mutations according to the direct plate incorporation method using Salmonella typhimurium strains TA 98, TA 100, TA 1535, TA 1537, and TA 1538 in both the presence and absence of S9 prepared from Aroclor-induced rat liver. Strain-specific positive controls were: sodium azide and 2-aminoanthracene (TA100 and TA1535); 2-nitrofluorene and 2-aminoanthracene (TA98 and TA1538); ICR-191 and 2-aminoanthracene (TA1537). All positive controls, solvent controls and test article were plated in triplicate. The experiment using TA 100 (-S9) was replicated due to unacceptable positive control values.

Treatment with SUPERFLOC HX-100 did not produce a dose related increase in the number of revertant colonies in any of the tester strains. Solvent and positive controls gave the expected results.

9.2.2 Micronucleus Assay in the Bone Marrow Cells of the Mouse (Ref No:)

9.3 Overall Assessment of Toxicological Data

Toxicological data were provided for SUPERFLOC HX-100 (a flocculant containing 5.2% of the notified polymer) although not required under the Act for a polymer with number-average molecular weight > 1000.

In animal studies, SUPERFLOC HX-100 had low acute oral (LD50 > 5000 mg/kg in rats) and low acute dermal (LD50 > 2000 mg/kg in rabbits) toxicity. It was a moderate to severe skin irritant (rabbit) but was not a skin sensitiser (mice). It was a moderate to severe eye irritant in rabbits.

There was no evidence from the Salmonella typhimurium histidine reversion test that SUPERFLOC HX-100 caused gene mutations.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Ecotoxicological data have been provided for SUPERFLOC HX-100, although not a requirement for polymers of number-average molecular weight > 1000 according to the Act. The following test results, obtained according to OECD Guidelines 201 (11), 202 (12) and 203 (13) were provided for aquatic species (4).

Test	Species	Result
Acute toxicity toxicity toxicity inhibition	Rainbow trout Bluegill sunfish Daphnia magna S. capricornutum	LD_{50} (96h) = 380 mg.L ⁻¹ LD_{50} (96h) = 280 mg.L ⁻¹ LC_{50} (48h) = 1.5 mg.L ⁻¹ EC_{50} (96h) = 2.2 mg.L ⁻¹

The above results indicate that Superfloc HX-100 is practically nontoxic to fish but is moderately toxic to aquatic invertebrates and algae. The 96 hour no observable effect level for the algal toxicity test was $2.0~{\rm mg.L^{-1}}$, indicating a steep toxicity curve. Algal toxicity is most probably due to the ability of poly

acrylic acid to chelate nutrient elements (14) required for algal growth.

US EPA has not recorded daphnia toxicity for this type of polymer. Closer scrutiny of the daphnia acute toxicity results shows that there were no observable effects at mg.L⁻¹, the 24 hr LC50 is > 1.8 mg.L⁻¹ (highest concentration tested) and that significant mortalities were found only in a repeat of the 48 hr 1.8 mg.L⁻¹ test. These findings suggest some caution should be exercised with the acute toxicity to daphnia result.

Further hydrolysis of the polymer would lead to a higher proportion of poly (acrylic acid) units and formation of hydroxylamine which is known to be toxic to aquatic organisms (Daphnia LC50 = 1.2 mg.L-1, Fathead minnow LC50 = 7.2 mg.L⁻¹ and S. capricornutum EC50 inhibitory = 1 mg.L⁻¹) (15).

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

There will be significant environmental exposure of the polymer in the product Superfloc HX-400 flocculant at the alumina refinery. The notified polymer will be mixed with mud daily in the solid separation and water recycling process and will ultimately be left bound with dried mud on extensive evaporation flats adjacent to the alumina refining plant.

The recycled water from the two dam mud separation system is likely to contain some notified polymer but will be contained in the closed water recycling process at the refining plant.

Both lakes/dams and the drying beds are operated with a safety margin which allows for receipt of emergency waste dumping and a minimum of 1 in 100 year storm events. This safety factor is expected to alleviate concerns of the notified polymer being released to the aquatic environment through overflow of the dams. The concentration of notified polymer in the dams can not be reliably estimated as the quantities of substance bound to mud or remaining in the supernatant are not known.

The user of the notified substance has obtained approval from Western Australian authorities for this process. Ground water around the mud flats is monitored in order to detect any contamination that would arise from penetration of the plastic

and clay liners. Results are reported to the Western Australian authorities.

12. <u>ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY</u> <u>EFFECTS</u>

The notified chemical is a high molecular weight polymer (> 1000) in a water-in-oil emulsion. The polymer is therefore unlikely to cross biological membranes and is expected to pose a low health hazard. The polymer is expected to contain no polymeric species below 1000 molecular weight. However, it contains hazardous impurities at levels above their cut-off values for the classification as a hazardous substance (16) and therefore caution must be exercised by workers when handling the polymer.

SUPERFLOC HX Series emulsions, such as SUPERFLOC HX-400 and SUPERFLOC HX-200, are stable at ambient temperatures, are non-flammable, have no explosive properties and are not expected to react with other materials. However, they contain a number of hazardous additives. Additionally, SUPERFLOC HX-100 emulsion (containing ~5% polymer) has been shown in animal studies to be a moderate to severe skin and eye irritant. With appropriate engineering controls, however, these emulsions should not pose a significant hazard to workers. Public exposure should be low given the use pattern of the emulsion and the final concentration of the polymer at the user's tailing dams.

Based on the above information, it is considered unlikely that SUPERFLOC HX Series emulsions will pose a significant hazard to public or occupational health and safety when used in the proposed manner.

13. RECOMMENDATIONS

To minimise occupational exposure (and public/environmental if recommendations have been made by these agencies) to SUPERFLOC HX Series Flocculant the following guidelines and precautions should be observed:

. Engineering control procedures such as local exhaust ventilation should be used to meet component occupational exposure limits (17) as described in MSDS for SUPERFLOC HX-

400 during manufacturing or refinery processes. Where feasable, closed systems should be used.

- . Suitable personal protective equipment which complies with Australian Standards should be worn such as chemical-type goggles with face shield recommended to prevent eye contact (18), chemically resistant gloves (19) and protective clothing (20) to prevent skin contact.
- . Good work practices should be implemented to avoid splashing or spillages.
- . Good personal hygiene practices, such as washing of hands prior to eating food, should be observed.
- A copy of the MSDS for products containing the notified polymer in water-in-oil emulsion, such as SUPERFLOC HX-400 and SUPERFLOC HX-200, should be easily accessible to employees working with products containing the chemical.

14. MATERIAL SAFETY DATA SHEET

The Material Safety Data Sheet (MSDS) for SUPERFLOC HX-400 Flocculant (Attachment 1) was provided in Worksafe Australia format (21). This MSDS was provided by Cyanamid Australia Pty Ltd as part of their notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of Cyanamid Australia Pty Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals* (Notification and Assessment) Act 1989 (the Act), secondary notification of SUPERFLOC HX Series Flocculant 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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 Toxicology: Salmonella typhimurium, Reverse Mutation Assay
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- 20. Australian Standard 3765.1-1990 Clothing for Protection against Hazardous Chemicals Part 1 Protection against General or Specific Chemicals Standards Association of Australia Publ, Sydney, 1990.
- 21. National Occupational Health and Safety Commission, Guidance Note for Completion of a Material Safety Data Sheet, 3rd Edition, Australian Government Publishing Service Publ., Canberra, 1991.